
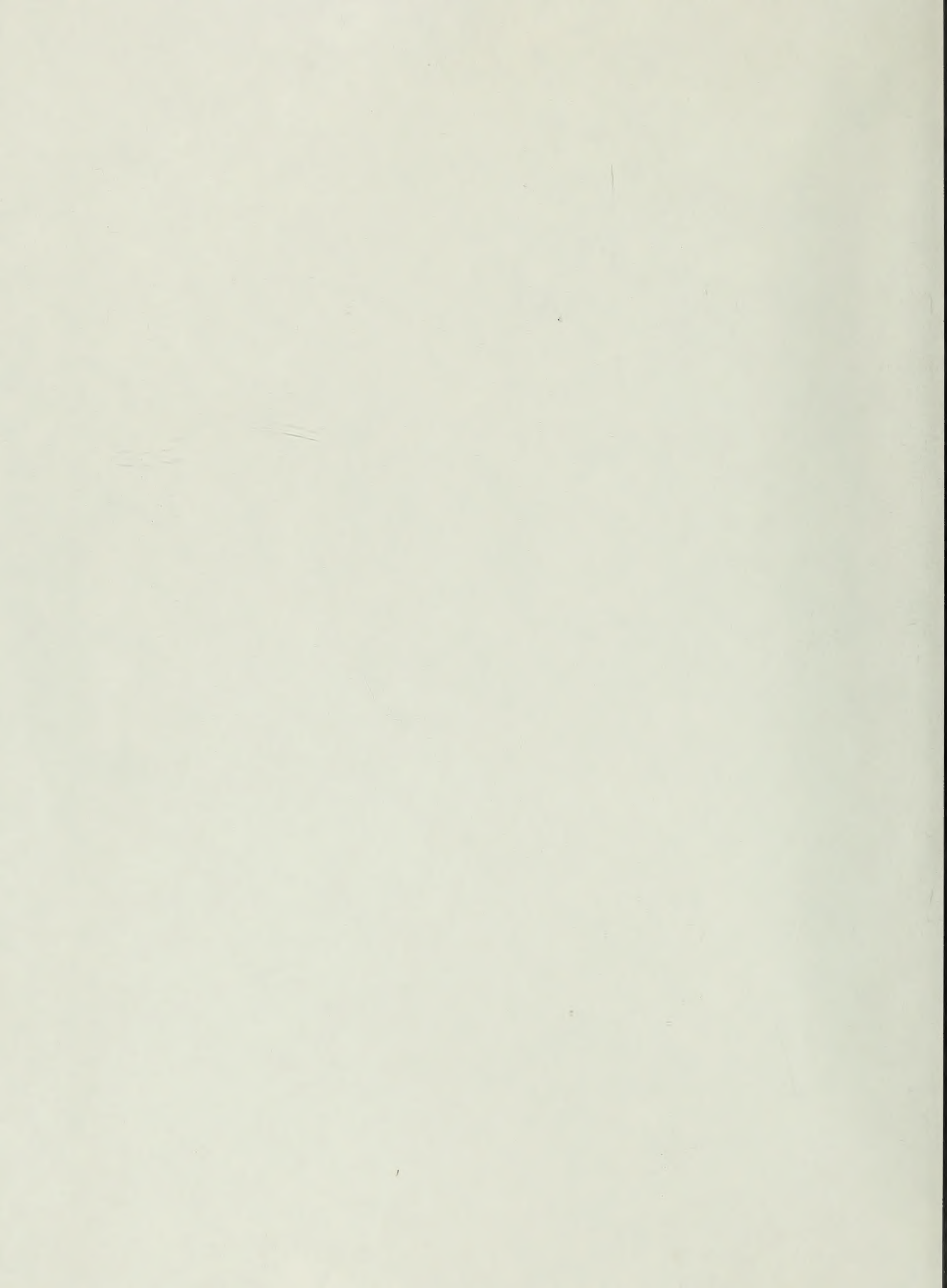



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Nuclear Quadrupole Resonance Studies of Cobalt(III) Complexes

Robert A. LaRossa

July 2, 1973

One of the most interesting outgrowths of research on the properties of Vitamin B₁₂ and its derivatives resulted from the observation that biochemically important forms, called coenzyme B₁₂ and methylcobalamin, exist in which there are direct cobalt-carbon bonds. This prompted the synthesis of a number of simple cobalt(III) complexes containing alkyl groups directly bound to cobalt. Among the most extensively studied molecules of this type are the Lewis base adducts of methylatobis(dimethylglyoximate)cobalt(III) ("cobaloximes").

Since nuclear quadrupole resonance (nqr) spectroscopy is a sensitive indicator of the electron distribution around a quadrupolar nucleus, a study of ⁵⁹Co and ³⁵Cl nqr in cobaloximes and related complexes should provide information pertinent to the question of bonding in these compounds. Prior to this study, ⁵⁹Co nqr had been observed in only a limited number of six-coordinate Co(III) compounds. The observed transition frequencies were generally below 12 MHz. Therefore, a nuclear quadrupole resonance spectrometer of the superregenerative type, which had optimum sensitivity in this low frequency region, was developed and used to detect most of the resonances reported in this seminar. ⁵⁹Co and ³⁵Cl quadrupole coupling constants and ⁵⁹Co asymmetry parameters were determined for a series of compounds XCo(dh)₂L, where dh = dimethylglyoxime monoanion, X = CH₃⁻, Cl⁻, Br⁻, CHCl₂⁻, L = Lewis base. ⁵⁹Co chemical shifts were also measured for most of the compounds in this series.

A description of the generation and orientation of the ⁵⁹Co field gradient tensor in terms of d-orbital populations is only partially successful. However, by using a "donated charge" model and taking the geometry of the complexes into account, it is possible to determine how the quadrupole coupling constant and asymmetry parameter should change as the interactions with the ligands X and L change. Taken in conjunction with the ⁵⁹Co nmr shifts, the measured nqr parameters may be interpreted in terms of this model.

CHEMISTRY AND BONDING IN SUBSTITUTED COBALT CARBONYL COMPLEXES

Thomas E. Boyd

August 17, 1973

The study of metal-metal bonding among the transition metals is a relatively new development. In this research, three types of compounds were investigated: (1) dimeric compounds of the form $[\text{Co}(\text{CO})_3\text{P}]_2$; (2) heteronuclear metal-metal bonded compounds of the type $\text{R}_3\text{MCo}(\text{CO})_3\text{P}$; and (3) compounds having a higher degree of phosphorus base substitution. In these systems, M represents a group IV metal, R is an organic group, and P denotes a phosphine or phosphite.

Previous work has established that the dimers, $[\text{Co}(\text{CO})_3\text{P}]_2$, consist of two axially substituted tetracarbonyl cobalt moieties joined by a cobalt-cobalt bond. This is not true of the $\text{P}(\text{OCH}_2)_3\text{CC}_2\text{H}_5$ derivative, however, in which the phosphorus ligands occupy radial positions. The electronic spectra of these compounds were investigated in oriented nematic phase to determine the polarization of absorptions observed between 350-400 nm. These appear to be polarized along the cobalt-cobalt bond which is consistent with their assignment as $\sigma \rightarrow \sigma^*$ transitions. These studies showed that cobalt-cobalt bond strength is dictated by the effective σ -donor strength of the phosphorus ligands. From the ^{59}Co nqr spectra, the nuclear quadrupole coupling constant, eQq , was found to increase as the Lewis basicity of the phosphorus ligands decreased. In terms of the populations of the cobalt 3d orbitals as expressed by the equation

$$q_{zz} = q_{320} [N_{d_{z^2}} + \frac{1}{2}(N_{d_{xz}} + N_{d_{yz}}) - (N_{d_{xy}} + N_{d_{x^2-y^2}})]$$

in which q_{zz} is the electric field gradient (efg) at cobalt and q_{320} is the efg arising from a $3d_{z^2}$ electron, a decrease in Lewis basicity decreases the $N_{d_{z^2}}$ term causing a lowering of q_{zz} and thus eQq . This is a valid conclusion, as previous work has shown the $(N_{d_{xy}} + N_{d_{x^2-y^2}})$ term to be larger than the sum of the other two terms. The insertion of SnCl_2 into the cobalt-cobalt bond at 60°C exhibited a dependence of reaction rate upon bond strength. However, the exact nature of this dependence is uncertain as the reaction mechanism has not been elucidated.

In the investigation of the heteronuclear metal-metal bonded compounds, the group IV metal, the group IV metal substituents, and the phosphorus base were varied to assess the effects of these changes on the metal-cobalt bond. These compounds have a trigonal bipyramidal structure with the group IV metal moiety and the

phosphorus ligand occupying the axial positions. Spectroscopic changes resulting from the variation of the group IV metal were too small to provide for rigorous interpretation. However, when the substituents of these metals were varied, the electronic spectra showed a dramatic increase in metal-cobalt bond strength as the electronegativity of these groups decreased. The electronic, infrared, and nqr spectra showed a lesser degree of change when the phosphorus ligand was varied. As the π -acceptor strength of the phosphorus ligand increases, there is an observed increase in metal-cobalt bond strength. Distortion of the three-fold symmetry was noted in the nqr and infrared spectra when the axial moieties were substituted with bulky substituents such as phenyl, for example.

Compounds of the type $(\text{C}_6\text{H}_5)_3\text{SnCo}(\text{CO})_{4-x}\text{P}_x$ in which $x \leq 2$ were investigated. The electronic spectra revealed that the tin-cobalt bond strength decreases upon substitution of one carbonyl group by a phosphorus ligand, but increases when a second one is introduced. Among the disubstituted compounds, two isomers are possible. The fact that there was only one set of nqr resonances and no observed broadening or splitting in the infrared spectra support the notion that one isomer is present. Based on our knowledge of the monosubstituted compounds, the disubstituted species have a phosphorus ligand in the axial position and one of the radial positions. Attempts to prepare compounds having a higher degree of phosphorus ligand substitution were unsuccessful.

LIGAND EXCHANGE STUDIES OF METHYLATOCOBALT(III) COMPLEXES

Randolph J. Guschl

August 24, 1973

Variable temperature ^{19}F and ^1H nmr studies have been obtained to determine the rates of axial base exchange from complexes of the type $\text{CH}_3\text{Co}(\text{chel})\text{B}$, where chel represents a planar tetradentate chelate and B is a donor base. For the base 1-(2-trifluoromethylphenyl)imidazole (Im-CF_3), nmr spectra in the region of intermediate exchange were observed and matched with computer-generated lineshapes for chel = N,N'-ethylenebis(acetylacetonate) (bae), bisdimethylglyoximate ($(\text{dh})_2$), diacetylmonoximeimino-diacetylmonoximateimino-propane-1,3 (tmed), 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (tim), and the ring system found in the heptamethyl ester of cobyrinic acid (cobester). From the calculated lineshapes, first-order rate constants for dissociation were evaluated and comparative ΔG^\ddagger values were computed. The order of base lability reflects a cis effect of electron donation by the chelate in the order $\text{bae} > \text{cobester} > (\text{dh})_2 > \text{tmed} > \text{tim}$.

Base adducts of the alkylcobalt(III) complexes of $(\text{dh})_2$, tmed, and tim were prepared to observe the effect of replacing the -OHO-groups of $(\text{dh})_2$ with $-(\text{CH}_2)_3-$ moieties. Interactions of these systems with THF, CH_3OH , $\text{S}(\text{CH}_3)_2$, $\text{N}(\text{CH}_3)_3$, 3-fluoropyridine, Im-CF_3 , $\text{P}(\text{OCH}_3)_3$, and acetonitrile in nitrobenzene and methylene chloride were observed and the relative ordering of dissociation rates was found to depend on the nature of both the base and the chelate. For any one base, exchange is fastest when the chelate is $(\text{dh})_2$ and slowest with tim. This is discussed in terms of changes in the charge at the cobalt center and the subsequent changes in σ and π -interactions.

The rate of dissociation of $\text{P}(\text{OCH}_3)_3$ from $\text{CH}_3\text{Co}(\text{dh})_2\text{P}(\text{OCH}_3)_3$ was observed in solvents of varying dielectric constant, and the rate at 100°C was found to decrease by a factor of about 2 over the range of solvents from toluene to nitrobenzene. Replacement of protons in the -OHO- bridges of the planar ligand system by deuterium results in no observable change in $\text{P}(\text{OCH}_3)_3$ dissociation rate. A limiting S_N1 mechanism for dissociation has been proposed involving a transition state which is less polar than the ground state, and which does not differ much from the ground state in geometry.

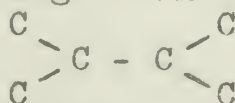
The kinetics data are discussed in terms of a strong cis effect of the chelate, and the biological implications of this study are explored. The rate of exchange of Im-CF_3 from the Im-CF_3 adduct of methylatocobester was found to be 30.0 sec^{-1} at 49°C . The result implies that axial base exchanges in all alkylcobalt(III) corrinoids are rapid enough to allow base exchange during or before the Co-C cleavage characteristic of mechanisms involving these systems.

STRUCTURAL AND BONDING PROPERTIES OF SMALL RING COMPOUNDS

Yu Wang

August 20, 1973

A problem which has excited a great deal of interest during the past several years has been the chemistry and bonding of three and four center systems. We have studied the bonding charge distributions and structural properties in three- and four-membered ring systems containing the second row elements: A three-membered ring compound, tetracyanocyclopropane (TCCP), was studied both by X-ray diffraction and photoelectron spectroscopy. In this compound, half of the C-C≡N groups were found to be non-linear and the (CN)₂C-C(CN)₂ fragment was found to be non-planar. A comparison of this compound with transition metal olefin complexes¹ will be made. The charge distribution in the molecule calculated from photoelectron spectroscopic data showed that there is a positive charge region in



which is susceptible to nucleophilic attack.

A four-membered ring compound, squaric acid, was studied both by X-ray and neutron diffraction. Assuming D_{4h} symmetry, the aromatic oxocarbon dianion of squaric acid, C₄O₄²⁻, has an unusually large amount of stabilization energy.² The squaric acid structure is planar and forms an infinite sheet by means of strong inter-molecular hydrogen bonding. Due to the tetragonal pseudosymmetry, the solution of the structure proved to be difficult. With the assistance of the single crystal infrared and Raman data,³ the space group was determined to be P2₁/m with two molecules per unit cell. The molecular geometry displays neither D_{4h} symmetry nor a discrete 1,2-dione structure. Rather, the π-electrons are extensively delocalized through the solid by means of hydrogen bonding. Thus, shifting the positions of the hydrogen atoms results in the formation of tautomeric isomers. In order to understand more about the squaric acid aggregate and the extensive π-delocalization, dimethylammonium hydro-bis-bi-squarate, [(CH₃)₂NH₂·H₃(C₄D₄)₂], was synthesized and studied by X-ray diffraction. As in squaric acid, strong inter-molecular hydrogen bonding occurs. However, in the squarate fragment of the ammonium salt, both symmetric and non-symmetric hydrogen bonding are found.

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BONDING AND STEREOCHEMICAL STUDIES OF
GROUP IA AND IIA ORGANOMETALLIC COMPOUNDS

Richard Zerger

August 23, 1973

In the past there has been some question as to whether or not hydrogen atoms are an integral part of the bonding in metal-carbon-metal bridge bonds.^{1,2,3,4} In our attempt to answer the question the synthesis and structural investigation of several bicyclobutyl-organometallic compounds were undertaken. The complex bicyclobutyllithium TMEDA was found to be a dimer with bridging bicyclobutyl groups. This structure represents the first example of a solvated oligomeric alkyl lithium compound and the first example of a tertiary carbon electron deficient compound. The existence of a tertiary carbon in a bridging position demonstrates that hydrogen involvement is not necessary for the formation of alkyl-metal bridge bonds. The bonding and structural properties of bis-bicyclobutyl-mercury as exemplified by proton nmr will also be discussed.

The interaction of the fluorenyl anion with alkali metal cations has been rather extensively investigated.^{5,6,7,8,9,10} Brooks and co-workers¹¹ determined the X-ray structure of fluorenyllithium bisquinuclidine and interpreted their results in terms of some directed covalent bonding. They also predicted that in the other fluorenyl-alkali metal complexes containing alkali metals other than lithium, the alkali metal position will be determined to a greater extent by the electrostatic potential of the carbanion. In order to evaluate the validity of this prediction, the X-ray structural analysis of fluorenyl-potassium TMEDA was undertaken. The complex was found to be polymeric in character with chains of alternating anions and cations. The general aspects of

the structure can be explained by the above electrostatic model with some features which may be due to either steric effects or a degree of directed valence bonding.

Fischer and Stolzle¹² prepared biscyclopentadienylcalcium by the reaction of calcium metal with cyclopentadiene in THF. The unsolvated $(C_5H_5)_2Ca$ crystallized in a space group different than that reported for $(C_5H_5)_2Mg$ and $(C_5H_5)_2Fe$, suggesting the possibility of an unusual metal environment. With the hope of obtaining further information about the interaction between the cyclopentadienyl rings and the calcium cation, the X-ray analysis of $(C_5H_5)_2Ca$ was undertaken. The coordination sphere around the calcium was found to consist of two $h^5-C_5H_5$ rings, one $h^3-C_5H_5$ ring, and one $h^1-C_5H_5$ ring. The first three rings are disposed about the calcium atom in a roughly trigonal manner with the fourth ring approximately perpendicular to the plane formed by the centroids of the other three rings.

The structure of cyclohexyllithium was determined by X-ray analysis and found to be a hexamer. The geometry of the molecule consists of a cluster of six lithium atoms with the cyclohexyl rings bonded to six of the eight triangular faces. This structure is the same as that predicted for an alkyl lithium by Brown¹³ in 1962. The bonding proposed for cyclohexyllithium is based on the four-centered bond theory.

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NUCLEAR MAGNETIC RESONANCE STUDIES OF ORGANOMETALLIC EXCHANGE REACTIONS

Richard L. Kieft

August 24, 1973

Mixtures of alkyllithium and lithium tetraalkylaluminates were prepared in diethyl ether and their ^7Li and proton nmr spectra obtained. Variable temperature ^7Li studies were done when R = methyl and ethyl. The slow exchange region was reached by -50°C when R = methyl and by -57°C when R = ethyl. When R = trimethylsilylmethyl (TMSM), ^7Li exchange is fast at -95°C . The rate determining step for this exchange is the dissociation of the alkyllithium tetramer into dimers. Detailed lineshape analysis for these systems yielded activation energies for the dissociation of the lithium tetramer of $12.4 \text{ kcal-mole}^{-1}$ when R = methyl and $11.3 \text{ kcal-mole}^{-1}$ when R = ethyl. The activation energy when R = TMSM would be even lower indicating that the more electron donating alkyl groups promote the dissociation of the alkyllithium tetramer.

Variable temperature proton nmr spectra were obtained for high ratio mixtures of $\text{MeLi}:\text{LiBr}$. The slow exchange region for this system is reached by -50°C . Detailed lineshape analysis yields a much higher activation energy than that obtained in the MeLi-LiAlMe_4 system, indicating that the rate-determining step is not the dissociation of the methyllithium tetramer. A new mechanism involving the dissociation of the mixed tetramer, $\text{Li}_4\text{Me}_3\text{Br}$, into the dimers Li_2Me_2 and Li_2MeBr is proposed for this system. Lineshape analysis yields a value of $16.5 \text{ kcal mole}^{-1}$ for the activation energy.

Proton and ^7Li nmr studies were done on solutions containing various mixtures of $(\text{TMSM})\text{Li}$ and $(\text{TMSM})\text{Cu}$. Spectra were obtained over the temperature interval of $+40^\circ\text{C}$ to -100°C . The results indicate that $\text{LiCu}(\text{TMSM})_2$ is the only complex formed in solution, but they do not reveal the extent of aggregation for $\text{LiCu}(\text{TMSM})_2$.

Attempts were made to prepare complexes between 2-methallyl-lithium and bis-(trihapto-2-methallyl)nickel, but only the coupling product, 2,5-dimethyl-2,5-hexadiene, was obtained. The reaction of (trihapto-2-methallyl)nickel bromide dimer with carbon monoxide was examined. Infrared spectra failed to show any evidence of a dicarbonyl intermediate, $(\text{h}^3\text{-C}_4\text{H}_7)\text{NiBr}(\text{CO})_2$, similar to that found in the analogous trihaptocyclopropenyl system. The reaction of (trihapto-2-methallyl)nickel bromide dimer with 1,2-bis(diphenylphosphino)-ethane, diphos, yields the five-coordinate compound $(\text{h}^3\text{-C}_4\text{H}_7)\text{NiBr}(\text{diphos})$. Nmr spectra for this compound were found to be similar to those of the analogous palladium compound, indicating that there is no motion of the allyl protons leading to exchange on the nmr time scale up to 100°C .

A MOLECULAR ORBITAL DESCRIPTION OF LEWIS ACID-BASE
INTERACTIONS
(Final)

Allen Marks

September 4, 1973

An equation for correlating enthalpies of adduct formation has recently been developed. The equation has the form:

$$-\Delta H = E_A E_B + C_A C_B \quad (1)$$

where E_A and C_A are empirical parameters assigned to a specific acid and E_B and C_B are empirical parameters assigned to a specific base. Several correlations between thermodynamic and spectroscopic properties have also been found recently, as well as correlations between E and C parameters and various molecular properties. Therefore, it was of interest to develop a molecular model of acid-base interactions with which the E and C parameters may be interpreted.

The particular model chosen to represent the acid-base interaction is that of the Mulliken charge transfer model. The enthalpy of adduct formation is given by the energy of the initial state, before interaction (minus the ionization energy of the base, I_B) minus the energy of the final state, after interaction (given by the energy of the lower energy "complex" orbital). The resultant equation is

$$-\Delta H = \frac{H_A + H_B}{1-S^2} + \frac{2SH_{AB}}{1-S^2} + \frac{2\sqrt{((H_A - H_B)/2)^2 + R_A R_B}}{1-S^2} - 2I_B \quad (2)$$

where $H_1 = \int \psi_1 \hat{H} \psi_1 d\tau$

$$H_{AB} = \int \psi_A \hat{H} \psi_B d\tau$$

$$S = \int \psi_A \psi_B d\tau$$

$$R_1 = H_{AB} - SH_1$$

For the particular case of reactions of neutral acids and bases such as



the enthalpies of adduct formation are quite small. Under these circumstances approximations for some of the terms in equation (2) can be made which simplify it to an equation similar to equation (1). It is found that the $E_A E_B$ product represents the energy of electrostatic interactions between A and B whereas the $C_A C_B$ product represents the energy gained by covalent bonding in the A:B molecule.

For the particular base of reactions of ionic acids and bases such as



the enthalpy of adduct formation is very large. Therefore, different approximations from the ones used above must be used to simplify equation (2). This treatment results in a new equation of the form:

$$-\Delta H = \sqrt{(D_A - D_B)^2 + O_A \cdot O_B} \quad (3)$$

where D_A and O_A are empirical parameters assigned to a specific acid and D_B and O_B are empirical parameters assigned to a specific base.

Equation (3) is used to correlate enthalpies of interaction of ionic acids and bases. Reactions of divalent acids and bases with monovalent and divalent bases and acids, respectively, are also included. A comparison is made between equations (1) and (3) in their ability to correlate enthalpies of reactions of both neutral and ionic acids and bases.

THE REACTIVITY AND MAGNETOCHEMISTRY OF SELECTED METALLOCENES (Final)

Mary Ellen Switzer

September 10, 1973

The rate of ring exchange of first transition series metallocenes with LiC_5D_5 was studied by a near-infrared technique. Mass spectra of nickelocene isolated from the exchange reaction verify that the entire cyclopentadienyl group, rather than individual hydrogens, exchanges; the spectra show only peaks corresponding to $\text{Ni}(\text{C}_5\text{H}_5)_2$, $\text{Ni}(\text{C}_5\text{H}_5)(\text{C}_5\text{D}_5)$ and $\text{Ni}(\text{C}_5\text{D}_5)_2$. For $\text{M}(\text{C}_5\text{H}_5)_2$ the rate of exchange decreases in the order $\text{Cr, Mn} > \text{Ni} > \text{V} \gg \text{Fe, Co}$. The cobalt and iron compounds show no exchange with LiC_5D_5 in four weeks or more. Of the first transition series metallocenes only manganocene exchanges rings with $\text{Ni}(\text{C}_5\text{D}_5)_2$. The relative reactivity of the metallocenes toward ring exchange parallels their reactivity toward nucleophilic substitution and can be explained in terms of the donor or acceptor properties of the metallocenes.

Since the rate of exchange of nickelocene is the most favorable for study, the kinetics of its reaction with LiC_5D_5 , the tetramethylethylenediamine (TMEDA) adduct of LiC_5D_5 and $\text{Mn}(\text{C}_5\text{H}_5)_2$ were investigated. A two-term rate law is observed for the reaction of lithium cyclopentadienide with $\text{Ni}(\text{C}_5\text{H}_5)_2$. One term is first order in each reactant; the other is second order in LiC_5D_5 and first order in $\text{Ni}(\text{C}_5\text{H}_5)_2$. The rate law is interpreted as parallel reactions of monomeric and dimeric lithium cyclopentadienide. In THF at 25-35° the dimerization constant is $\leq 10^{-1}$. At 30° in THF the rate constants for exchange with nickelocene are $4.56 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$ ($\Delta H^\ddagger = 11.0 \pm 3.3 \text{ kcal mole}^{-1}$ and $\Delta S^\ddagger = -40 \pm 11 \text{ e.u.}$) for lithium cyclopentadienide monomers and $\geq 1.5 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ ($\Delta H^\ddagger = 13.8 \pm 1.8 \text{ kcal mole}^{-1}$ and $\Delta S^\ddagger = -28 \pm 6$) for the dimer.

We found that LiC_5D_5 forms a 1:1 complex with TMEDA. The reaction of nickelocene with this complex follows a simple second-order rate law, with $k = 1.17 \times 10^{-1} \text{ M}^{-1} \text{ sec}^{-1}$ at 27° ($\Delta H^\ddagger = 11.5 \pm 0.7 \text{ kcal mole}^{-1}$ and $\Delta S^\ddagger = -31.7 \pm 2.7 \text{ e.u.}$).

Manganocene and magnesium cyclopentadienide exchange rings slowly with nickelocene. The manganocene exchange follows a second-order rate law, $k = 4.35 \times 10^{-6} \text{ M}^{-1} \text{ sec}^{-1}$ at 30° ($\Delta H^\ddagger = 15.3 \pm 0.89 \text{ kcal mole}^{-1}$ and $\Delta S^\ddagger = -30.5 \pm 2.8 \text{ e.u.}$). If the $\text{Mg}(\text{C}_5\text{H}_5)_2$ exchange is also second order, $k < 4.8 \times 10^{-6} \text{ M}^{-1} \text{ sec}^{-1}$ at 55° . All of these ring exchange reactions are interpreted in terms of an associative mechanism in which the coordinative ability of the cyclopentadienyl group is lower in the transition state.

Manganocene and 1,1'-dimethylmanganocene were studied in detail. Their ionic properties include adduct formation with a variety of Lewis bases and ring exchange with nickelocene.

The nmr data show that there is some covalent character to the metal-ring bond in manganocene. For dimethylmanganocene the bonding is covalent enough for the low-spin state to become important. The existence of the $S = 1/2$ state has been deduced from the temperature-dependent magnetic moment of dimethylmanganocene. At 30.5° the magnetic moment in benzene is 4.76 BM, well below the spin-only value of 5.92. At 4.2°K esr experiments show that the ground state is 2E ($g_{||} = 2.922$, $g_{\perp} = 1.893$ in methylcyclohexane glasses). The existence of a 2A state at 138°K in a toluene glass is inferred from the isotropic g value at this temperature. The low spin 2A state is used as a tentative explanation of the large downfield shifts in the nmr of dimethylmanganocene at 310°K (-137 and -77 ppm in benzene for the ring and methyl resonances, respectively).

SPECTROSCOPIC STUDIES OF PENTA-COORDINATE ORGANOMETALLIC COMPLEXES

Cheryl D. Pribula

September 13, 1973

Isoelectronic penta-coordinate complexes $[M(CO)_5-xP_x]^n$, where $P = P(C_6H_5)_3$ or $P(OCH_3)_3$, and $M = Mn$ ($n = -1$), $Fe = 0$ ($n = 0$), or Co ($n = +1$), have been studied using nqr, Mössbauer, ir and nmr spectroscopy.

Small changes in metal valence electron distribution are reflected by the field gradient at the metal nucleus, eq_{zz} . This parameter was determined from nqr (^{55}Mn , ^{59}Co) and Mössbauer (^{57}Fe) experiments for a number of complexes.

To a good approximation, eq_{zz} is given by

$$eq_{zz} = eq_{320}[N_{d_{z^2}} + 1/2(N_{d_{xz}} + N_{d_{yz}}) - (N_{d_{xy}} + N_{d_{x^2-y^2}})] + eq_{410}[N_{p_z} - 1/2(N_{p_x} + N_{p_y})] \quad (1)$$

The N's are orbital populations, usually approximated by Mulliken population analysis methods. Values of eq_{320} and eq_{410} , which are the field gradients due to a single electron in a $3d_{z^2}$ and $4p_z$ orbital, respectively, were calculated for the metal ions $Mn(-1)$, $Fe(0)$, and $Co(+1)$ in different electron configurations. Although it has usually been assumed that the p-orbital contribution is insignificant, we have shown that this term is comparable in magnitude with the d term. For $Fe(CO)_5$, eq_{zz} was evaluated from equation (1). The results are in good agreement with the experimental field gradient. Relative values of eq_{320} for the three metal ions are compared with relative values of eq_{zz} observed for $[Mn(CO)_5]^-$ and $Fe(CO)_5$ and estimated for the hypothetical $[Co(CO)_5]^+$. It is concluded that the populations of the planar d orbitals increase, relative to the axial, in the order $Mn < Fe < Co$.

The effect of phosphorus ligand substitution on eq_{zz} was examined. For positive eq_{zz} (known for the Fe complexes and assumed for Mn and Co), substitution of the stronger σ -donating poorer π -accepting (relative to CO) P ligand should lower eq_{zz} by increasing the populations of d_{z^2} and $d_{xz,yz}$. Actually a simple trend is not observed, and the results are not easily interpretable.

Infrared spectra of $LiMn(CO)_5$ and $NaMn(CO)_5$ in the CO stretching region have been examined in ether solvents. The spectra are attributed to an ion-paired species of C_{3v} symmetry in which alkali metal is bonded to carbonyl oxygen. Treatment of $NaMn(CO)_5/THF$ with Mg^{2+} gives a species whose ir is consistent with a $Mg-OC$ interaction.

The complex $[\text{Co}(\text{CO})_2(\text{P}(\text{OCH}_3)_3)]^+$ was examined from -105° to $+40^\circ$ using several different nmr techniques. The room temperature pmr spectrum indicates rapid intramolecular exchange, while at -105° , exchange is apparently slow. The complexity of the spin system precludes mechanistic analysis. Other techniques, ^{31}P -decoupled ^1H nmr and ^1H -decoupled ^{31}P nmr, produce fast exchange spectra even at low temperatures. At 30° , the ^{13}C nmr exhibits a very broad carbonyl resonance due to ^{59}Co - ^{13}C interaction, although at lower temperatures this effect is negligible. A method of decoupling ^{59}Co must be devised if ^{13}C is to be useful in mechanistic studies.

KINETICS AND MECHANISMS OF THE SUBSTITUTION REACTION OF ALKYL-
GROUP IV METAL COBALT-TETRACARBONYLS

James Eaton

September 18, 1973

The reaction of $\text{Ph}_3\text{MCo}(\text{CO})_4$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$) was studied in the presence of phosphine bases. The rate of reactivity was shown to depend on both the incoming base and the acidity of the group IV metal. The rate of reactivity was $\text{Si} \gg \text{Ge} > \text{Sn}$. The reaction was shown to obey the rate law:

$$\text{rate} = k_2[\text{L}][\text{Ph}_3\text{MCo}(\text{CO})_4]$$

where L is the Lewis base concentration.

Several correlations were made between the acidity of the group IV metal and the rate of reaction. Based on this, the initial step in the mechanism was proposed to be base attack at the group IV metal.

The silicon reaction was studied quite extensively in order to determine the complete mechanism. When the base was $\text{P}(\text{C}_4\text{H}_9)_3$, the initial product was $[\text{Ph}_3\text{Si}_2\text{P}(\text{C}_4\text{H}_9)_3]^+[\text{Co}(\text{CO})_4]^-$. This rearranged upon standing to give the final product $\text{trans-Ph}_3\text{SiCo}(\text{CO})_3\text{P}(\text{C}_4\text{H}_9)_3$. This reaction was not affected by the presence of excess CO. On the other hand, when the base was PPh_3 , no ion pair was detected. The product again was $\text{trans-Ph}_3\text{SiCo}(\text{CO})_3\text{PPh}_3$. The presence of excess CO caused the rate of this reaction to slow down. Based on these observations, a mechanism was proposed. It involved base attack at the group IV metal followed by ion pair formation. This ion pair then recombined to give a reactive intermediate in which cobalt was coordinatively unsaturated. This intermediate then rearranged to yield the final product.

The rate constants measured involve only the base attack at the group IV metal. This is, however, the rate determining step.

ELECTRON TRANSFER REACTIONS OF COBALT COMPLEXES

Michael Broccardo

September 18, 1973

The decrease in the specific rate of outer-sphere electron transfer reactions observed when ammonia ligands in the inner-coordination sphere of a transition metal ion are replaced by ethylenediamine has generally been explained as due to the greater size and steric bulk of the latter ligand. However, hardly any systematic effort has been directed toward studying complexes containing saturated ligands bulkier than ethylenediamine with the purpose of determining if such ligands are able to further reduce the specific rate of electron transfer, i.e. to serve as "electron insulators". Therefore, in this study the outer-sphere electron transfer reactions of $\text{Co}(\text{chxn})_3^{3+}$ (chxn = trans-1,2-diaminocyclohexane) and $\text{Co}(\text{en})_3^{3+}$ (en = ethylenediamine) with a common reductant have been examined in detail.

The observed rate constants at 25°C and associated activation parameters for the reactions of $\text{Co}(\text{chxn})_3^{3+}$ and $\text{Co}(\text{en})_3^{3+}$ with $\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{2+}$ in aqueous 0.10 M Cl^- media are $k = 3.8 \times 10^{-3}\text{ M}^{-1}\text{ sec}^{-1}$, $\Delta H^\ddagger = 17.6 \pm 0.5\text{ Kcal/mole}$, $\Delta S^\ddagger = -10.6 \pm 1\text{ e.u.}$ and $k = 6.2 \times 10^{-3}\text{ M}^{-1}\text{ sec}^{-1}$, $\Delta H^\ddagger = 17.1 \pm 0.5\text{ Kcal/mole}$, $\Delta S^\ddagger = -11.3 \pm 1\text{ e.u.}$, respectively. The actual reductant in this system is shown to be $\text{Ru}(\text{NH}_3)_5\text{Cl}^+$.

For V^{2+} as the reductant in aqueous $0.10\text{ M CF}_3\text{CO}_2^-$ media, the specific rate constant and associated activation parameters for $\text{Co}(\text{chxn})_3^{3+}$ are $k = 5.8 \times 10^{-4}\text{ M}^{-1}\text{ sec}^{-1}$, $\Delta H^\ddagger = 14.8 \pm 0.9\text{ Kcal/mole}$, and $\Delta S^\ddagger =$

-25.4±2.9 e.u.; and for Co(en)_3^{3+} , $k = 9.6 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$, $\Delta H^\ddagger = 14.2 \pm 0.3 \text{ Kcal/mole}$, and $\Delta S^\ddagger = -26.4 \pm 0.9 \text{ e.u.}$

It is concluded that the mere size or bulk of the ligand coordinated to the cobalt(III) metal center has only a small effect upon the rate of outer-sphere electron transfer. In addition, the lack of any significant difference in ΔS^\ddagger for the two oxidants suggests that the reactions of Co(chxn)_3^{3+} are not dramatically less adiabatic than those of Co(en)_3^{3+} .

The second part of this report examines the rate of outer-sphere electron exchange between the cobalt clathro chelates, $[\text{Co}^{\text{III}}(\text{dmg})_3(\text{BF})_2]^+$ and $[\text{Co}^{\text{II}}(\text{dmg})_3(\text{BF})_2]$, in which the central cobalt ion is coordinated to three dimethylgloxime (= dmg) ligands through six nitrogen atoms. Numerous earlier investigations have demonstrated that the rates of outer-sphere electron transfer between cobalt(III) and cobalt(II) complexes are quite slow in comparison with the rates of self-exchange between analogous complexes of other transition metals.

Since octahedral cobalt(II) complexes are usually high-spin with a 4T ground state while cobalt(III) complexes are almost always low-spin with a 1A ground state, this anomalous behavior has frequently been attributed to the changes in spin multiplicity which occur with electron transfer. As both of the cobalt clathro chelates are low-spin species, the self-exchange electron transfer reaction is "spin-allowed", i.e. electron exchange can take place without a spin multiplicity change on either reactant in the activated complex except for the transferred electron.

Although the exact value for the rate of self-exchange was not determined, it was demonstrated via exchange broadening of the nmr spectrum of the diamagnetic cobalt(III) complex that $k_{ex} < 400 \text{ M}^{-1} \text{ sec}^{-1}$ at 80° in nitromethane. This is not appreciably faster than the rates of electron transfer observed for cobalt(III)-cobalt(II) systems which are "spin-forbidden", i.e. which involve a spin-multiplicity change. It is concluded that outer-sphere cobalt(III)-cobalt(II) self-exchange reactions are inherently slow because of the considerable coordination-sphere and solvation-sphere reorganization energies which accompany transfer of an anti-bonding electron and not because of spin multiplicity changes.

OXIDATIVE DEHYDROGENATION AND KINETICS OF
RUTHENIUM(II)-ETHYLENEDIAMINE COMPLEXES

Dennis Mahoney

October 5, 1973

Oxidative dehydrogenation of large macrocyclic ligands has been known to occur for a number of years. More recently it has been found that small bidentate ligands such as ethylenediamine and even monodentate ligands such as methylamine may also react in this fashion. In all cases the ligand remains coordinated throughout the process:



Here M(II) represents a divalent metal whose valence state remains unchanged and en and diim refer to ethylenediamine and its diimine analog.

In the studies reported here the oxidation of ruthenium(II)-ethylenediamine complexes was studied as a function of the acid strength and the reduction potential of the complex. The complexes studied included Ru(en)_3^{2+} ($E^\circ = +0.19\text{V}$), $\text{Ru(en)}_2\text{phen}^{2+}$ ($E^\circ = +0.55\text{V}$), and $\text{Ru(phen)}_2\text{en}^{2+}$ ($E^\circ = +0.76\text{V}$). Oxidation will yield either the ruthenium(III)-ethylenediamine complex or the ruthenium(II)-diimine complex depending on the acid strength. As the reduction potential of the complex becomes (numerically) larger, stronger acid strengths are required to prevent oxidative dehydrogenation. Participation of the metal in the oxidative dehydrogenation process is also implied by the cyclic voltammetry of the complexes. As the E° increases the potential required to induce oxidative dehydrogenation increases but is always higher than that ne-

cessary to reversibly oxidize the metal. These results are in accord with those found in macrocyclic compounds wherein the metal is first oxidized and is then reduced in attacking the ligand.

In the second part of the study the electron transfer rate of $\text{Ru(en)}_2\text{diim}^{2+}$ reacting with Fe^{3+} was investigated in an effort to determine the effects of ligand conjugation on electron transfer rate. The rate is found to be much slower than that of the saturated analog, Ru(en)_3^{2+} , under the same conditions. The results are discussed in terms of the Marcus Theory of Electron Transfer. The difference is shown to be due to a substantially larger free energy change in the latter case. It is concluded that the effect of conjugation is small, at least in these systems, due to the high transmission coefficients present, even in the saturated systems.

BIOCHEMICAL APPLICATIONS OF LANTHANIDE SHIFT REAGENTS

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November 20, 1973

INTRODUCTION

The application of lanthanide shift reagents (LSR's) to nmr spectroscopy has proven to be an important outgrowth of the more general usage of paramagnetic shift reagents.¹ In the few years since Hinckley² first systematically applied the LSR's to nmr spectral clarification, the field has rapidly expanded and now includes such applications as determination of optical purity, elucidation of conformation and structure of compounds in solution, dynamic nmr spectroscopy and the most frequently employed simplification of complex, overlapping spectra.³⁻⁷ LSR's have been used most extensively in resolving spectra of organic molecules and more recently have been applied to organometallic molecules and biological model systems.

THEORY^{8-12, 12a}

The LSR interacts with the compound to be studied by coordinating with donor atoms of the molecule, thus forming a new complex in solution. This coordination effects a "shift" in the nmr spectrum of the compound of interest by inducing a large local magnetic field due to the unpaired electronic spin of the paramagnetic lanthanide ion. Variations in the local magnetic field introduce additional magnetic non-equivalences of the surrounding nuclei.

The shift consists of a contact and a pseudocontact contribution. In the case of the lanthanide ions, the pseudocontact contribution predominates.

Structural and conformational studies in solution have made use of the predominance of the pseudocontact interaction in the lanthanide ions in that the pseudocontact mechanism depends directly on the magnetic anisotropy of the complex formed and on geometric factors between the metal ion and the coordinated nuclei.

Added structural information may be gained through the use of certain LSR's as broadening or relaxation reagents. Lanthanides with this broadening ability possess a long electronic relaxation time as compared to the molecular reorientation times.

BIOCHEMICAL APPLICATIONS^{13, 22-24}

Since extensive application has been made of LSR's to studies of conformation and structure of organic compounds in solution, a natural outgrowth of this area has been consideration of biologically important molecules. Much recent work has been done on conformational studies of mono- and dinucleotides in solution.¹⁴⁻¹⁶ The intent of such studies is to derive information on the effect of environmental conditions on the conformation of molecules in order to be able to predict and rationalize the conformation of molecules in biological systems once the conditions of the local biological environment are known.

One of the more significant applications of LSR's over the last few years has been their use as probes of membrane structure.¹⁷⁻²¹ Most of this work has been done on model membrane systems consisting of sonicated phospholipid bilayers. NMR techniques using paramagnetic ion probes have been able to differentiate between the internal and external phospholipid monolayers.

In biological membranes the added presence of lipoproteins very likely produces an asymmetric distribution of the various phospholipid classes in the two surfaces of the membrane. The ready associability of solvated paramagnetic ions with lipid polar headgroups in lipid vesicles provides a potential method for determining the distribution of lipid classes in the surface of biological membranes.

Enzymatic activity may be very dependent on the binding of the protein and/or the substrate in the lipid bilayer. There may also be a correlation between the motional factor in the lipid bilayer and enzymatic activity. Since both relaxation and shift reagents supply information on distance and orientation relative to the phosphate head groups and the membrane surface, lanthanide ions should prove to be particularly well-suited to such studies as the above.

Other contexts in which the LSR's should serve to be applicable include studies of electron transport intermediates, the structure and conformation of metalloproteins and the mechanism of transport of various molecules through cell walls.

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NUCLEAR RELAXATION PROCESSES: APPLICATIONS

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Although the theory for nuclear spin relaxation has been known since 1948,¹ measurement of relaxation times was difficult until the advent of Fourier transform nmr instruments. The three relaxation times, T_1 , T_2 , T_2^* , are measured as follows:

$$1/T_2^* = \pi \nu_{1/2}$$

($\nu_{1/2}$ is the line width at half maximum intensity of a normal absorption spectrum.)

T_1 by a pulsed experiment using a $(180^\circ - \tau - 90^\circ)$ sequence or a $(\pi - 90^\circ - \pi - 180^\circ - \tau - 90^\circ)$ sequence.

T_2 by using a $(90^\circ - \tau - 180^\circ)$ sequence.

There are five types of interaction which contribute to T_1 and T_2 :^{2,10}

1. magnetic dipole-dipole
2. spin rotation
3. chemical shift anisotropy
4. electronic quadrupole
5. scalar coupling of the first and second kind

Each interaction gives rise to fluctuating magnetic fields which couple the spin system to the lattice. This is expressed by the matrix element

$$(s | A F(t) | s' | r') = (s | A | s') (f | F(t) | f')$$

(where f and f' are lattice functions, s and s' are spin functions, A is a spin operator and $F(t)$ is a lattice operator. A and F depend on the interaction involved.)

Using the appropriate matrix element and the standard method for calculation of transition rates, one obtains the expression for the rate of relaxation by each interaction. These expressions are given below for when the extreme narrowing condition is met.

magnetic dipole-dipole³

$$(1/T_1)_{\text{rot}} = (1/T_2)_{\text{rot}} = \frac{2\gamma^4 I(I+1)}{r^6} \tau_c$$

$$(1/T_1)_{\text{trans}} = \frac{\rho}{3} \gamma^4 h^2 I(I+1) \frac{Nn}{kT}$$

chemical shift anisotropy⁴

$$1/T_1 = \frac{2}{15} \gamma^2 H_0^2 (\sigma_{11} - \sigma_{\perp})^2 \tau_c$$

$$1/T_2 = \frac{2}{15} \gamma^2 H_0^2 (\sigma_{11} - \sigma_{\perp})^2 \tau_c$$

spin rotation

$$1/T_1 = 2\pi \frac{1 \cdot kT}{h^2} C_{\text{eff}}^2 \tau_r$$

electric quadrupole

$$1/T_1 = 1/T_2 = \frac{3}{40} \frac{2\pi}{h^2} \frac{1}{I^2(2I-1)} \left(1 + \frac{\tau_c^2}{T^2}\right) \left(\frac{e^2 Q q}{h}\right)^2 \tau_c$$

scalar coupling of the first kind

$$1/T_1 = \frac{2}{3} A^2 S(S+1) \left[\frac{\tau_e}{1 + (\omega_I - \omega_S)^2 \tau_e^2} \right]$$

$$1/T_2 = \frac{A^2}{3} S(S+1) \left[\tau_e + \frac{\tau_e}{1 + (\omega_I - \omega_S)^2 \tau_e^2} \right]$$

scalar coupling of the second kind replace τ_e with τ_S .

Applications

The applications of nuclear relaxation times have recently been reviewed.⁵

J. Jagur-Grodzinski, et al., studied the complexation reaction of sodium ions with crown ethers in various solvents using ^{23}Na nmr spectroscopy. There is almost no change in the chemical shift of ^{23}Na upon complexation by the crown ether. However, complexation could be observed by noting the difference in T_2 due to quadrupole relaxation.⁶

In 1966, T. R. Steagle and J. D. Baldeschwieler proposed the use of mercuric chloride to probe the sulfhydryl sites in proteins and to determine the correlation time of the bound halide. Later, E. J. Wells, et al., showed that using mercuric bromide as the probe permitted one to gain kinetic data relating to the halide mercury exchange.^{7,8}

^{13}C T_1 measurements have been used to determine a specific electron-nuclear relaxation rate which is used for investigating solvent-solute interaction with paramagnetic $\text{Cr}(\text{acac})_3$ and to follow segmental motion in carbon chains.

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MANGANESE PORPHYRINS AND PHTHALOCYANINES

Lynne M. Parr

February 5, 1974

Metals are essential elements in a number of biological processes. Their role ranges from trigger and control mechanisms to structural contexts and redox catalysis.¹ Manganese is present in many of these roles. Many enzymes require manganese, and a few manganese-containing proteins are known.²

One of the important roles of manganese is in the oxygen evolutionary process of photosynthesis.³ The nature of the manganese complex in the chloroplast is unknown, however, it may be a porphyrin or chlorophyll-like molecule. Model studies have thus been undertaken on these types of systems in an effort to understand the role of manganese in photosynthesis.

MANGANESE PORPHYRINS^{4,5,6}

Manganese porphyrins are most stable as Mn(III). These complexes contain a complexed anion, exhibit no ESR signal, and have a magnetic moment indicative of a high-spin d^4 complex. The electronic spectrum of the Mn(III) porphyrin complexes is unusual. No Soret band is observed. Rather, the spectrum consists of six bands whose positions vary with the porphyrin ligand used, the solvent, and the anion.

The Mn(III)-porphyrins may be reduced to the corresponding Mn(II)-porphyrin, or oxidized to the Mn(IV)-porphyrin. The redox potentials vary markedly with pH and porphyrin. Some of the reduction potentials are large enough to cause the oxidation of water.

The manganese porphyrins are similar to the iron porphyrins in many ways. They also exhibit some unique differences. Many of the differences arise from the fact that Mn(III) is only found in the high-spin state.

MANGANESE PHTHALOCYANINES^{7,8,9}

These complexes are similar to the porphyrins in many ways. They do, however, exhibit some interesting differences. The chemistry of these complexes is quite extensive. An oxo-bridged species has been investigated and has sparked considerable controversy.

The observed chemical behavior of these groups of compounds has led to a proposed mechanism for the evolution of oxygen from plants during photosynthesis.

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THE ACTIVE SITE OF MEMERYTHRIN

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Introduction

Hemerythrin is an oxygen carrier pigment found in some invertebrate phyla: sipunculids, polychaetes, priapulids, and bachiopods. This pigment is known to exist as an octamer. Each subunit or monomer which contains two non-heme iron atoms reversibly combines with one oxygen molecule.¹ To elucidate the structure of the active site of hemerythrin, particularly the oxidation states of the two iron atoms and their relative positions as well as that of ligands coordinating to the metal, magnetic susceptibility measurements, U.V., visible, C.D., O.R.D.,^{2,3,4} Mössbauer, and resonance Raman spectroscopies, and amino acid sequential, compositional and reactivity analyses have been employed.⁵

Deoxyhemerythrin

In deoxyhemerythrin the iron atoms seem to exist as magnetically independent high-spin iron(II) according to Mössbauer and magnetic susceptibility measurements.^{6,7} The two iron atoms can either combine with an oxygen molecule forming oxyhemerythrin, or be oxidized by an oxidizing agent such as potassium hexacyanoferrate(III) and then combine with one or two ligands forming methemerythrin.⁸

Oxyhemerythrin

Oxyhemerythrin could be considered as either two iron(II) atoms combined with an oxygen molecule or two iron(III) atoms combined with a peroxy ion. The spectroscopic and magnetic measurements support the latter, where two high-spin iron(III) are strongly antiferromagnetically coupled.^{6,7,9,10,11} Iron Mössbauer spectra of oxyhemerythrin show two doublets indicating that there are two non-equivalent iron atoms in a subunit, while only one type of iron is observed in Mössbauer spectra for deoxy- and methemerythrin.¹²

Methemerythrin

Methemerythrins have been subject to active investigations, though they are not naturally occurring active forms of this protein. In this class of compounds, two high-spin iron(III) atoms are also strongly antiferromagnetically coupled.^{10,11} Anions such as azide, thiocyanate, cyanide, isocyanate, bromide, chloride, fluoride, and hydrosulfide are known to form complexes with an iron to anion ratio of 2 to 1, in which the two iron(III) atoms are indistinguishable in iron Mössbauer spectra.^{7,12} This implies that the anions may be bridging the two iron atoms in a symmetrical manner. Water, hydroxide, and fluoride ions coordinate to iron in the ratio 1 to 1.¹³

Coordinating Groups

Since hemerythrin does not contain any heme group, the coordination sphere of the iron atoms has to be completed by amino acid side chains, water or other small molecules or ions. Chemical modification of amino acid side chains by specific reagents indicates that there are four slow-reacting histidine and two slow-reacting tyrosine residues.^{14,15,16,17} The only cysteine residue found in a subunit is not coordinated to iron.¹⁸ The terminal as well as ϵ -amino group of the lysine residues are also believed not to be the coordinating group.¹⁴ Comparison of amino acid sequences of hemerythrin from different species could be a powerful method to find out the essential residues for the active site. Sequences of two hemerythrins, that of *Dendrostomum pyroides* and *Golfingia gouldii* are known, but they are too close to each other for this purpose.^{19,20,21,22}

Model Systems

From magnetic and Mössbauer evidence, μ -oxo high-spin di-iron(III) compounds have been proposed as a model system of the active site of the oxygen carrier protein. Based on this model, several spectroscopic features of hemerythrin have been predicted, but they have not been unambiguously proved due to hindrance by the protein absorption bands.²³ Several structural models for oxyhemerythrin have been suggested to explain the non-equivalence of the two iron sites. However, there is no definitive evidence for any of the models.^{11,13}

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HOMOGENEOUS INORGANIC OSCILLATING REACTIONS

Ben Fieselman

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Periodic fluctuations in the measurements of quantities such as concentrations, absorbance, electric potential, and the rate of gas evolution have been reported in a significant number of chemical reactions.¹ Glycolysis in yeast cells,² hydrocarbon combustion,³ dissolution of chromium in hydrochloric acid, and numerous other widely varying types of reactions produce oscillations. Only within the last few years have studies begun to explain the causes of oscillations and the mechanisms.⁴ The relative ease of collecting data and the availability of relevant kinetic studies make homogeneous inorganic oscillating reactions the most favorable systems for studying the general phenomena of oscillation in chemical systems.

Thermodynamic Considerations

The thermodynamics of oscillating systems have well developed by physicists and mathematicians.¹ Oscillating reactions proceed with a net reaction and a decrease in Gibbs free energy.⁵ Unlike reactions which monotonically approach equilibrium, oscillating systems fluctuate around quasi-steady state equilibria as they advance slowly toward true equilibrium. As long as a reaction moves toward true equilibrium, there is no restraint that prevents oscillation in the concentrations of intermediates; however, oscillation about true equilibrium is theoretically forbidden.

Kinetics of Oscillation

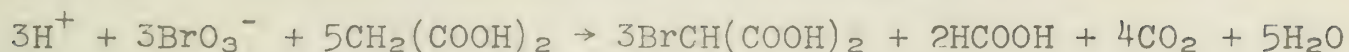
The kinetics of oscillating systems can be described as the coupling together of several separable reactions. One prerequisite for oscillation in a chemical system is an autocatalytic step that functions as a feedback switch to turn on and off the reaction step giving rise to the observed fluctuations.⁷ The reactions must be far from equilibrium for oscillations and must approximate an open system in which reactants effectively come from a large reservoir and products are deposited into a sink.⁸ Rate constants for individual steps must fall within certain limits to allow the required coupling of reactions.

The theoretical possibility of undamped chemical oscillations was first proposed by Lotka in 1920.⁹ With the advent of computers, rate expressions derived from numerous theoretical mechanisms have been shown to predict periodic fluctuations in concentrations.¹⁰

Belousov Reaction

The best understood homogeneous oscillating reaction is the Belousov reaction.¹¹ When a bromate salt is mixed with the required concentrations of cerium(III) and malonic acid in an aqueous sulfuric acid solution, oscillations occur in bromide and cerium(III) concentrations. Temperature gradients and spatial oscillations have been

reported.¹² The net reaction is the following:¹³

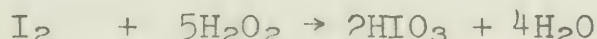


Noyes and coworkers proposed a ten step mechanism for the Belousov reaction that is consistent with observed periodic changes in concentrations, with available redox potentials, and with kinetic studies in other laboratories.¹¹ Their method was to break the full reaction into appropriate phases and to consider independently each phase. The mechanism includes a free radical branching step that is autocatalytically inhibited by the presence of bromide. Oscillations are sustained by the alternation of the inhibition as the bromide concentration changes.

Despite the elegant mechanism, it is not possible to deal fully quantitatively with the Belousov reaction because of the insolvable form of the general rate expression. Approximate rate expressions can be derived for specific portions of a given cycle.¹¹ Attempts have been made to computer simulate several proposed mechanisms that could be found in any oscillating reacting.¹⁴ By supplying rate constants and initial concentrations, it is possible to establish whether a particular mechanism generates oscillations.¹⁰ Computer and mathematical methods for treating oscillating reactions lag behind the level of complexity required to deal with actual laboratory results.

Bray Reaction

In 1921 Bray reported that a mixture of hydrogen peroxide, potassium iodate, and sulfuric acid in the appropriate concentrations showed oscillations in the rate of oxygen evolution.¹⁵ Oscillations in the concentrations of iodine, iodide, and hydrogen ion have been identified.¹⁶ The Bray reaction appears to involve the following reactions:¹⁷



The mechanism is not known, but it has been proposed to involve a radical chain autocatalytic step that is activated and then inhibited to produce oscillations.¹⁷ At present, the identity of the intermediates is an open question whose answer should allow an explanation for the periodic fluctuations.

General Conclusion

Free radicals are probably involved in many of the oscillating reactions in the autocatalytic step.¹⁸ In addition to the Bray and Belousov reactions, free radicals are probably significant in the little studied oscillating dithionite decomposition reaction.¹⁹ There are probably many more oscillating reactions to be discovered. The lack of interest in oscillating reactions and the need for instrumentation capable of continuous monitoring of concentrations explains why few systems are known. Biological enzyme systems, which abound with feedback controls (allosteric enzymes), are the most likely class of reactions to have oscillations.²⁰ It should eventually be feasible to design inorganic oscillation reactions.⁵

The knowledge gained from the study of oscillating systems should be of significance in understanding biological periodicity. Applications for oscillating reactions in industry and in further academic research remain to be defined.

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THE SPIN LABEL TECHNIQUE AND ITS ESR APPLICATIONS

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April 2, 1974

Introduction¹⁻⁸

A spin label is a synthetic, paramagnetic, site-directed, organic free radical. The first spin label back in 1965 was the cation radical of chlorpromazine,¹⁷ but the most successful compounds used as spin labels to date are nitroxide free radicals. The technique consists of introducing a spin label into the system of interest and observing the free radical by electron spin resonance spectroscopy. Information available from the esr spectrum includes polarity of environment, orientation and motion of the spin label, and proximity of two or more spin labels. Since the pioneering papers of H. M. McConnell in 1965, the spin label literature has grown to a prodigious size covering a wide range of applications to biological problems.

Theory^{2,4,6,7}

A very important feature of nitroxide spin labels is the comparative simplicity and high accuracy of the spin quantum mechanics that relates the physical state of the label to its paramagnetic resonance spectrum.² The electron spin resonance spectrum of a typical nitroxide in solution at room temperature is simple, consisting of three sharp lines produced by nitrogen hyperfine interaction. The g tensor and nitrogen hyperfine coupling tensor are solvent dependent^{9,10} and, thus, solvent effects can be used to probe the hydrophobic or hydrophilic nature of the environment around the label. The widths of the individual esr lines^{10,11} are markedly dependent upon the rotational mobility of the nitroxide. The general dependence of resonance spectra on the molecular motion of labels makes these paramagnetic molecules delicate indicators of conformation changes in macromolecules.²

Dinitroxide spin labels allow the study of certain intramolecular interactions, since the interaction between the two unpaired electrons of a biradical is a strong function of the conformation of the biradical. Although the electron-electron exchange parameter J is not easily related quantitatively to molecular geometry, the observation that an esr spectrum can be grossly altered by changes in structure or conformation renders J a potentially important parameter in spin labeling.¹²⁻¹⁵ The electron-electron dipole term can also, in principle, provide quantitative distance and conformational information in dinitroxide spin labeling experiments. The point dipole approximation has been used to relate the dipolar splitting to the distance between two nitroxides.¹⁶

Applications

It is convenient to group spin labels into three classes: (1) covalently binding spin labels, (2) noncovalently binding spin labels, and (3) spin-labeled analogs of biological molecules.

McConnell and co-workers^{1,18-22} took the approach of covalent attachment of an iodoacetamide spin label to alkylate cysteine β -93 of hemoglobin in their studies of the cooperativity of oxygen binding in hemoglobin. From several independent esr experiments, they obtained evidence that the protein structure in the vicinity of the spin label attached to β -93 depended on the state of oxygenation of the α -chains, thus, suggesting α - β subunit interactions.

Wood and co-workers^{23,24} synthesized an active spin-labeled cobinamide in order to elucidate the role of vitamin B₁₂ as a coenzyme. ESR was used to study the kinetics of the homolytic cleavage of the Co-C bond for these spin-labeled analogs of vitamin B₁₂.

One of the most popular applications of spin labels over the last few years has been their use as probes of biomolecular structure.^{4,6,7,15} Hubbell and McConnell²⁵ undertook an exploratory study of the structure of a number of biological membranes including the excitable membranes of nerve and muscle. They allowed a small unreactive nitroxide spin label to diffuse into several membranous systems. Interpretation and comparison of the characteristic esr spectra obtained for this paramagnetic probe in various systems led these workers to conclude that excitable membranes must contain either phospholipid bilayers similar to those present in phospholipid vesicles or other components with very similar hydrophobic regions.

Conclusion

As in all approaches involving molecular modification, one must consider to what degree a spin label alters the system. Although there are many examples of labeled systems maintaining the functions of the unmodified system, each system behaves differently. Thus, care should be exercised in interpreting spin label spectra. However, by careful choice of appropriate spin labels and labeling sites, it should be possible to study almost any desired system without significant structural perturbation.

One of the potentially most significant aspects of spin label spectra is that they can be observed in many situations--in protein single crystals, in solution, and in more complex structures such as membranes. The addition of this versatile technique to the battery of spectroscopic tools available to the biologist promises to add information in appropriately selected systems, which can be combined with information accumulating from other techniques.

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OBSERVING THE BEHAVIOR OF TRANSIENT CHEMICAL SPECIES

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April 11, 1974

Short-lived species, be they chemical intermediates or excited electronic states, may be studied by a variety of methods. Each of these methods has its own characteristic time domain. The limitations on the time domain may arise from either the uncertainty principle or may simply be due to experimental difficulties of the more practical and therefore avoidable sort.

Flash photolysis lies in this latter category. The problem in the past has always been to generate short enough pulses with sufficient intensity to observe the kinetically interesting, but short-lived species. New developments in laser technology have to some degree alleviated problems of this sort and it is now possible to generate pulses and observe spectral changes whose lifetimes are on the order of 10^{-11} sec.

Flash Photolysis

Here, the source of radiant energy is a gas discharge tube which is "fired" by shorting a condenser across the tube.¹ The wide choice of spectral regions and intensities accessible by using different tubes gives this technique good flexibility. The fundamental drawback has been the duration of the pulses. So-called "deconvolution" techniques allow the experimentalist to calculate lifetimes which are smaller than the duration of the flashes,² but this seems to be at best a second-order guess. Depending on the configuration of the apparatus, lifetimes on the order of 10^{-7} sec may be observed directly.

Q-Switched Lasers

Lasers offer several advantages over the conventional flash lamp. Better time resolution (10^{-9} sec vs 10^{-7} sec) is one, and they are also more efficient in delivering radiant energy to the sample. Thus, while flash lamps may generate hundreds or thousands of Joules of energy, much of this is wasted and a laser, though generating only 2-10 J, can produce a measurable effect by focusing all of it into the sample. The use of amplifying rods exterior to the laser is useful in these applications for providing additional power and transient concentrations. The use of frequency doubling³ provides some spectral flexibility, while optical delays and non-linear optical phenomena (white light⁴ generation) allow use of the laser for the dual role as source and monitor of the transient behavior.

Recent articles by Sutin⁵ detailing the use of these lasers as T-jump sources extends the flexibility for these particular systems. Thus, when the sample won't absorb at available frequencies, a solvent which does might be found.

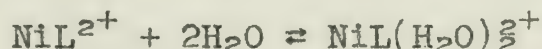
Mode-Locked Lasers

It is now possible to extend the range of measurable lifetimes down to the pico-second (10^{-12} sec) range.⁶ The power in such pulses is still very high (power=energy per unit time) even though the absolute energies are relatively low. The primary difference between this method and the two above is that the output consists of a series of pulses rather than just one pulse, so that experimental results are the sum of a number of separate experiments (assuming the system has recovered completely from one pulse before the next pulse arrives). Variation of the pulse separation is possible over the range from 2-10 nsec in practice.

Applications

Chlorophyll systems have now been studied by these techniques. Classical flash photolysis techniques are inadequate to resolve the fluorescence decay time.⁷ More sophisticated techniques using spark gap sources and photon counting equipment have been used to estimate lifetimes of from 0.6 to 1.6 n-sec without much apparent consistency.² The most recent measurement using a mode-locked laser, however, shows that there are probably two different fluorescing species and that the $1/e$ decay time is only 350 p-sec.⁸

Using a Q-switched laser system, various groups have examined the equilibrium



where L = N, N'-bis(2-aminoethyl)-1,3-propanediamine.^{9,10} Changing the incident frequency or the solvent made it possible to check the relative effects of the T-jump and photochemical perturbations. Even though these two perturbations push the equilibrium in opposite directions, the kinetic lifetimes were in close agreement, demonstrating the general validity of the interpretation of the photochemically obtained results in terms of the reactions of ground-state species.

The geometry of the photochemically generated metal pentacarbonyls of Cr, Mo and W have also been examined.¹¹⁻¹³ Early reports of the observation of the D_{3h} form presently appear to be in error.¹⁴ The absorption spectrum of the intermediate $\text{Cr}(\text{CO})_5$ is similar to that reported for $\text{Cr}(\text{CO})_5\text{THF}$, suggesting that the C_{4v} form is favored. This may be due to the ability of $\text{Cr}(\text{CO})_5$ to scavenge trace impurities¹³ in hydrocarbon solvents in order to satisfy its requirement for six-coordination. This high affinity for an octahedral structure may be related to the undesirability of the triplet ground state required in a $16e^- D_{3h}$ system.¹²

The reactions of I_2 in the presence of iodide in aqueous solution have also been studied using Q-switched lasers in the T-jump¹⁵ and photochemical excitation modes.¹⁶⁻¹⁸ In the former case, the very rapid equilibrium rate constants between I_2 and I_3^- have been measured. In the latter case, under the highest time resolution used, no direct evidence of the proposed I_2^- complex was observed, although good evidence for the existence of an I_2^- intermediate was presented.

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SECONDARY PROCESSES IN PHOTOELECTRON SPECTROSCOPY

Edward J. Laskowski

April 16, 1974

Until recently, the main thrust of research activity in X-ray Photoelectron Spectroscopy (ESCA) has been in the correlation of binding energies of inner core electrons with various parameters indicative of charge density such as Mossbauer chemical shifts,¹ oxidation states,² and the results of various molecular orbital calculations.³ These studies have all been concerned with the principal ionization lines and have ignored the less easily detectable and identifiable satellite lines.

The first step of the photoionization process is the creation of an inner shell hole by the interaction of the X-ray with the atomic electrons. Relaxation of outer orbitals takes place on a time scale which is long, compared with the photoejection, so that it is valid to consider the final state of the system as containing an inner orbital photohole. However, the electrons in the other shells can respond quickly to the inner shell hole by adiabatic orbital shrinkage. To a first approximation, the orbitals may be considered "frozen", and this effect neglected.⁴ Under the frozen-orbital approximation, energy transitions can arise only from electric monopole interactions and result in single electron ionizations. As a result, only transitions from well defined energy levels can occur, and hence the assignment of peaks to these levels. Within this approximation, additional structure can be introduced by two processes. These are: (1) Exchange splitting in open shell configurations, in which the final states differ in energy due to differing spin multiplicity,⁵ and (2) Multiplet splitting in which configuration interaction between a core level and a partially filled valence level gives rise to several energetically different states.⁶ Additional peaks can be observed due to the less interesting effects of nonmonochromatic excitation and impurities, especially metal oxides which form on the surface of the sample during irradiation.

Double electron excitation becomes allowed under the sudden approximation,^{7,8} in which the orbitals are no longer frozen. In this case, the photoionization is considered as a two step process in which the photoionization occurs, and then simultaneous excitation of a second electron results due to the change in the screening, together with the relaxation of the remaining electrons from neutral atom orbitals to ionized atom orbitals. If the process results in ionization of two electrons, it is referred to as shake-off, whereas if it results in the ionization of one electron and the promotion of a second electron to an excited state, it is referred to as shake-up.

A third two-electron process which is possible is Auger electron emission.⁹ This is a radiationless process in which an electron occupying a higher energy orbital relaxes to fill the photohole formed by the primary photoionization. Simultaneously with this relaxation, there is an ejection of a second electron. Although this gives rise to fairly intense peaks, this is not frequently studied due to the restrictions on the energy of the second ejected electron.¹⁰

ESCA studies of various transition metal carbonyls have been undertaken.¹¹ These spectra show distinct satellites, separated by 5-6 eV from the normal ionization peaks for C(1s) and O(1s) electrons. The metal center exhibits broadening of the principle ionization peak. These satellites have been attributed to shake-up due to charge transfer excitations, and indeed, the energy separations for the C(1s) and O(1s) satellites correspond well with the transition $1A_{1g}$ to d^1T_{1u} , which is the dominant feature in the UV absorption spectra of these complexes. From consideration of the differences between the UV dipole excitation and the ESCA monopole excitation,¹² the agreement between these two energies seems fortuitous and leads to the interpretation that the initial and final states are almost equally influenced by core ionization. The intensity variation suggests that the two electron excitation process is favored when the positive inner hole is located on the acceptor part of the molecule, since electron flow during the charge transfer process is favored towards this center. Likewise, the positive hole on the donor inhibits the charge transfer process, and hence the satellite is of low intensity at the metal site.¹³ Further evidence for this type of transition was given in a systematic study of substituted chromium carbonyls of the type $Cr(CO)_5X$, which revealed a reduction of the intensity of the oxygen satellite relative to the O(1s) ionization with increasing chromium-carbon bond strength.¹⁴ This is in agreement with a charge transfer excitation in the shake-up mechanism, as this should be inhibited by the presence of a strong electron donor on the metal center.

Recent studies of the satellite structure of 46 copper compounds¹⁵ and 70 nickel compounds¹⁶ have revealed features which are peculiar to the electronic configuration of the metal. It has been found that only paramagnetic metal centers give rise to satellite structure on the metal 2p signals. The 2p signals are split in all cases into a $2p_{3/2}$ component and a $2p_{1/2}$ component due to spin-orbit coupling. Three specific patterns of satellites arise in the paramagnetic centers: Type A, in which both 2p levels show two satellites; Type B, in which one 2p level shows two satellites and the other 2p level shows only one; and Type C, in which there is only one satellite associated with each 2p signal. Although the specific origin of these satellites is as yet uncertain, it has been suggested that the high energy satellite may be due to a shake-up transition localized on the metal center with excitations of the type 3d to 4s or 3d to 4p, while the lower energy satellite may be due to a shake-up transition of the type 3d to ligand antibonding orbital.

Possible application of these observations to structural chemistry has already been shown. In the case of $(K_2Ni(CN)_3)_2$, which is known to have Ni(I) paramagnetic centers, no satellites were observed, indicating that the metals were diamagnetic. X-ray diffraction studies have shown the compound to be dimeric and have a short metal to metal distance, indicative of a metal-metal bond, which is consistent with the ESCA data.¹⁶ The electronic structure of nickel dithiolate compounds was also clarified by the observation of ESCA satellites.¹⁷ These compounds were known to be paramagnetic, both in solution and in solid state. This was interpreted as indicating that the compounds

contained nickel (III) ions. Molecular orbital calculations indicated that the unpaired electrons were localized mainly on the ligand, however. The absence of shake-up satellites confirmed the latter interpretation.

Although the exact mechanism for multiplet splitting is still unclear, it appears that the observation of satellite lines will be useful in the interpretation of electronic structure, oxidation states, and stereochemistry. Hopefully, the problems with instrumental resolution can be solved, so that further progress can be made in this area.

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MAGNETIC EXCHANGE INTERACTIONS IN DIMERIC Cu(II) COMPLEXES.

(Thesis Seminar)

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April 18, 1974

In recent years, much attention has been given to the magnetic properties of binuclear transition metal complexes, in particular, the Cu(II) complexes.^{1,2} These systems can have either a direct metal-metal interaction^{3,4} or, the most common, an exchange interaction through bridging groups. In most cases, the exchange interaction is antiferromagnetic (singlet ground state),⁵⁻²¹ while a few compounds with a triplet ground state have also been observed.^{15,22-25} Usually, the bridging units are small molecules or ions, and the internuclear distances are not very large. Little esr work has been reported for these complexes, and the exchange mechanism has been treated in only a few of the systems.^{15,17,24,25}

The objective of this work was to synthesize dimer complexes from binucleating ligands with aromatic systems acting as bridging moieties in order to determine the possibility of exchange interactions in such systems. The compounds were characterized by analyses, infrared and either molecular weight determinations or mass spectrometry. The magnetic properties were studied by variable-temperature (4.2-290°K) magnetic susceptibility measurements and electron spin resonance.

Two kinds of binuclear complexes were studied: 1. Jäger-Type Complexes. These compounds were synthesized by a modified method of the reactions used by Jäger²⁶ in the preparation of monomeric square-planar complexes. The ligands formed from condensation reactions of a 6-diketone and the appropriate amine, either 1,2,4,5-tetraaminobenzene or 3,3',4,4'-tetraaminobiphenyl. 2. Schiff-Base Complexes. The ligands formed from condensation reactions of salicylaldehyde and the appropriate amine, either m-phenylenediamine, p-phenylenediamine²⁷ or 2,2',6,6'-tetraaminobiphenyl. The Cu(II) complexes for both types of compounds were prepared by reacting the ligand with Cu(OAc)₂·H₂O.

An intramolecular antiferromagnetic exchange interaction was found to be present in all of the Cu(II) complexes except when the bridging group is 3,3',4,4'-tetraaminobiphenyl. The strength of the exchange interaction was found to depend on such factors as type of orbital where the unpaired electron is present, internuclear distance and aromaticity of the bridging unit. The mechanism of exchange is explained in terms of delocalization of the unpaired electron of the Cu(II) ions into the aromatic bridging unit by means of overlap of the orbitals where the unpaired electron is present with the appropriate molecular orbitals of the ligand.

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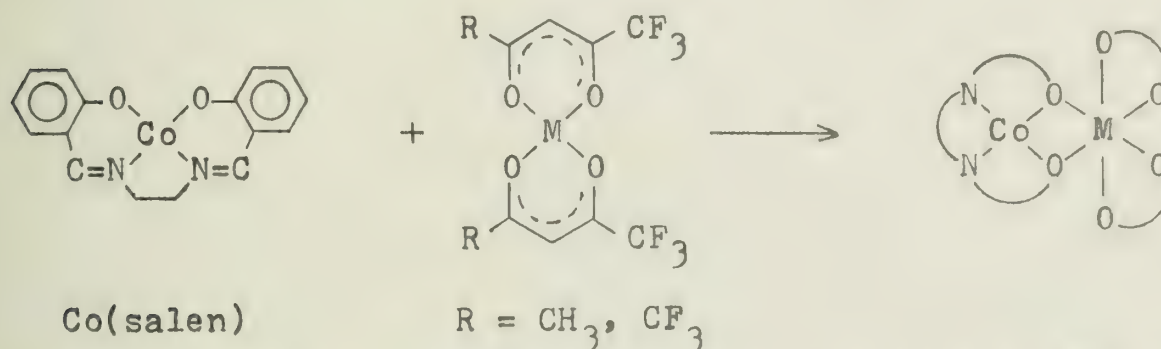
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BINUCLEAR COMPLEXES OF COBALT(II)

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April 19, 1974

The complex [α, α' -(ethylenedinitrilo)di-*o*-cresolato] cobalt(II), Co(salen), has been extensively studied as an oxygen carrier. Like its copper analog, Cu(salen) may also function as a bidentate ligand which in effect produces a binuclear complex with phenolic oxygen bridges. It has been found that with tri- or hexafluoroacetylacetone complexes of Ni^{2+} , Cu^{2+} , Zn^{2+} , and Cd^{2+} , Co(salen) does produce an adduct, the expected reaction being



The product illustrated above is formed if $\text{M} = \text{Zn}^{2+}$ or Cd^{2+} ; however, for $\text{M} = \text{Ni}^{2+}$ or Cu^{2+} the final product is best described as an adduct of M(salen) and Co(Facac)_2 , (Facac = fluorinated acetylacetonato), i.e., the two metals have exchanged coordination spheres. The fact that exchange has occurred in these cases is supported by magnetic susceptibilities and mass spectra.

The rate of metal exchange which is quite rapid when hexafluoroacetylacetone complexes are employed is significantly slower for the trifluoroacetylacetone analogs and does not occur at all for unsubstituted acetylacetone complexes. Kinetic studies of the trifluoroacetylacetone systems, while inconclusive in determining a rate expression or mechanism, do show that the reaction rate has a complex dependence on both reactant concentrations.

Molecular weight determinations, visible and ESR spectra show that the binuclear species undergoes negligible dissociation in non-coordinating solvents such as methylene chloride.

The crystal and molecular structure of the $\text{Cu(salen)Co(hfa)}_2$ adduct has been determined by X-ray diffraction (hfa = hexafluoroacetylacetonato). The structure, similar to that shown in the above diagram, contains a Cu^{2+} with square planar coordination and a Co^{2+} with a distorted octahedral environment. The copper-cobalt distance is 3.06 Å.

Solid state, room temperature magnetic susceptibilities indicate that when cobalt is in the salen moiety, its magnetic moment is approximately 2.8 BM, a high, but not uncommon moment for square planar Co^{2+} . If the cobalt atom is octahedrally coordinated, it is high spin with a magnetic moment of ~ 4.8 BM, a characteristic value for this type of environment.

The temperature dependence of the magnetic susceptibility of $\text{Ni(salen)Co(hfa)}_2$, which has only one paramagnetic center, was found to be quite ordinary over the temperature range 16-290°K: $\chi = 3.13/(T + 16)$. $\text{Cu(salen)Co(hfa)}_2$ gave a non-linear Curie-Weiss plot. Considerations of the susceptibilities indicate that some antiferromagnetic coupling may be present between cobalt and copper. However, low temperature ESR data is in apparent conflict with this hypothesis.

BONDING IN TRANSITION METAL BINARY HYDRIDES

Ma'mun Absi-Halabi

April 23, 1974

INTRODUCTION^{1, 2, 3}

Binary metallic hydrides are a wide class of metal-hydrogen compounds formed by the reaction of highly purified hydrogen with some of the transition metals and rare-earth elements in a pure form. The range of this class along with the other classes of hydrides known are shown in the accompanying periodic table.

Metallic hydrides exist in the form of brittle crystals, but they exhibit properties similar to those of metals,³ namely, thermal conductivity, electrical resistance, hardness and luster. They have a variety of applications in industry and, on a purely scientific level, they have unique properties compared to other hydrogen compounds.

This seminar will be limited to the nature of the bonding in this class, which has been a subject of controversy for a long time. The oldest model proposed was the solution of a gas in a solid where the hydrogen atoms occupy the interstitial sites of the metallic crystal without any form of electronic interaction with the metal atoms. This model had been rejected on the basis of the changes in crystal structure observed in some cases and the thermodynamic data obtained.

Since the development of atomic theory, two models of bonding have been mainly used in discussing the experimental results of metallic hydrides:

a) The Protonic Model^{1, 2, 4}

The hydrogen 1s orbital is assumed to be of higher energy than that of the Fermi surface of the metal. Consequently, the hydrogen atoms donate their electrons to the metallic bands and attain a (+1) oxidation state.

This model was able to account for the properties of palladium hydride, PdH_{0.6}, with some success.

b) The Anionic Model^{1, 2, 4}

The hydrogen 1s orbital is assumed to be of lower energy than that of the Fermi surface of the metal, thus it is assumed that it has a (-1) oxidation state.

This model was more widely accepted and was capable of accounting for a greater variety of the metallic hydride properties. Two other models have also been reported, the covalent bond model² and the intermediary model,⁴ but they were of more limited use.

AUGMENTED PLANE WAVE (APW) CALCULATIONS⁵⁻⁹

Recently, solid state quantum mechanical calculations were carried out on some transition metal hydride phases.⁵⁻⁸ The APW method⁹ used for the calculations is characterized by assuming an ideal potential, the muffin-tin potential, which is periodic and consists of two parts; a spherically symmetrical part that extends to a distance r from a nucleus, and a zero potential part throughout the region, r_1 - r_2 , between two spherical potentials of any two adjacent nuclei. The potentials were derived from Hartree-Fock-Slater coulomb potentials and charge densities of the hydrogen and the metal atoms. The crystal parameters used were those obtained from neutron diffraction and x-ray crystallography.

The results of these calculations show that the energy bands for the monohydrides are lowered considerably with respect to those of the metal. No new bands appear below the Fermi surface, although some states of the metal drop below it upon formation of the hydride phase. The lowest band of the hydride is a hybrid of the metal and the hydrogen s orbitals. Charge density calculations indicate that there exists a slight increase in electron density on the hydrogen of palladium hydride compared to the free hydrogen.

For the dihydrides, a new band, which is the antibonding combination of the two hydrogen 1s orbitals, appears below the Fermi surface. In addition, states that have the proper symmetry to interact with the hydrogen orbital are also lowered. The hydrogen atoms in this case are in a partially negative oxidation state.

The trihydrides treatment also shows that the hydrogen is in a partially negative oxidation state.

CONCLUSION

Although these calculations provide somewhat quantitative results in a unified way, more work should be done in order to resolve the remaining ambiguities and to provide a method for interpreting various trends.

A possible relationship between the electronic interactions in metallic hydrides and those in some other closely related areas, namely, catalytic hydrogenation and complex metal hydrides, is likely. This study of metal hydrides is an effort for the purpose of finding such a relationship that might lead to a better understanding of catalysis.

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Saline		Metallic										Covalent	
I A	II A											III B	IV B
LiH	(BeH ₂) _n Covalent											Series of Boron Hydrides	
NaH	MgH ₂											(AlH ₃) _n	Series of Si Hydrides
		III A	IV A	V A	VI A	VII A	VIII A			IB	II B		
KH	CaH ₂	ScH ₂	TiH ₂ (cubic and tetrag.)	VH VH ₂	CrH CrH ₂	Mn —	Fe —	Co —	NiH	CuH	(ZnH ₂) _n	(GaH ₃) _n	Series of Ge Hydrides
RbH	SrH ₂	YH ₂ YH ₃	ZrH ₂ (cubic and tetrag.)	NbH NbH ₂	Mo —	Tc —	Ru —	Rh —	PdH	Ag —	(CdH ₂) _n	(InH ₃) _n (InH ₃) _n	SnH ₄ Sn ₂ H ₆
CsH	BaH ₂	See Rare Earth Series	HfH ₂ (cubic and tetrag.)	TaH	W —	Re —	Os —	Ir —	Pt —	Au —	(HgH ₂) _n	(TlH ₃) _n (TlH ₃) _n	PbH ₄

LaH ₂ 3	CeH ₂ 3	PrH ₂ 3	NdH ₂ 3	Pm ?	SmH ₂ SmH ₃	EuH ₂	GdH ₂ GdH ₃	TbH ₂ TbH ₃	DyH ₂ DyH ₃	HoH ₂ HoH ₃	ErH ₂ ErH ₃	TmH ₂ TmH ₃	YbH ₂ YbH ₃ (?)	LuH ₂ LuH ₃
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AcH ₂	ThH ₂ Th ₄ H ₁₅	PaH ₃	UH ₃	NpH ₂ NpH ₃	PuH ₂ PuH ₃	AmH ₂ AmH ₃ (?)
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Binary hydrides formed by metals in the periodic table.

CALORIMETRIC STUDIES OF LEWIS ACID-BASE INTERACTIONS

R. Martin Guidry

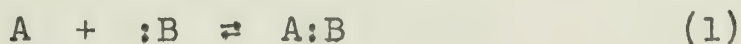
April 24, 1974

Introduction

The principal reason for a chemist to carry out structural studies is the potential importance of this information in understanding chemical reactions and chemical reactivity. Although techniques available for structural determination have improved considerably during the past decade, there has been few advances made during the past ten years in our understanding of chemical reactions and reactivity. A primary source of difficulty is the extreme complexity of typical chemical reactions--there are numerous energy terms contributing to chemical reactions which are not completely understood on the basis of the classical or quantum mechanical model. It is with this in mind that we have set out to study some of these energy terms. The initial step in this direction is the understanding of changes in the internal energy accompanying a very simple chemical reaction. The hope is that success will encourage study on more complex systems.

Discussion

A very simple reaction which is fundamental to a great number of complex reactions is the formation of addition compounds by Lewis acids and bases.



Over the past decade, a great deal of success has resulted from fitting the enthalpies of adduct formation ($-\Delta H$) for a large number of Lewis acid-base interactions to an empirical four-parameter equation^{1,2}--commonly called the E and C equation.

$$-\Delta H = E_A E_B + C_A C_B \quad (2)$$

E_A and C_A are empirical parameters for the Lewis acid and E_B and C_B are the corresponding parameters for the Lewis base involved in the reaction. By using the E and C equation, it is now possible to predict the enthalpies of over 1500 Lewis acid-base interactions--many of which are extremely difficult to measure experimentally.

When an attempt was made to obtain E_A and C_A parameters for the hydrogen bonding acid 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) by computer-fitting calorimetrically measured enthalpies of interaction of HFIP with various Lewis bases, the fit was much poorer than one would anticipate. Two possible sources of the poor fit were a steric hindrance problem between one or more of the adducts or some constant contribution to all the measured enthalpies. The steric hindrance problem appeared improbable for an acid as small as a proton. The difficulty was believed due to the demonstrated³ intramolecular hydrogen bonding in HFIP between the hydroxyl proton and $-CF_3$ fluorine. If this intramolecular bond has to be completely broken during the course of formation of the intermolecular Lewis acid-base bond, then this would comprise a constant contribution to the enthalpy. One

should then be able to subtract a constant amount from each of the experimentally measured enthalpies (which consist of two contributions--the breaking of the intramolecular bond and the formation of the Lewis acid-base bond) to obtain the enthalpy of the Lewis acid-base bond. This constant amount would represent the enthalpy of the intramolecular hydrogen bonding in HFIP. When this procedure was attempted, a best-fit of the E and C equation to the experimentally measured enthalpies was obtained when the constant amount was $-1.1 \text{ kcal mole}^{-1}$. In order to simplify the procedure and obtain error limits for the value of the constant contribution, the E and C equation was modified to incorporate the constant contribution (W) and a computer program was written to solve for the three unknown parameters (E_A , C_A and W),

$$-\Delta H = E_A E_B + C_A C_B + W \quad (3)$$

Upon solving Equation 3 for the HFIP-Lewis base systems, it was found that the enthalpy of the intramolecular hydrogen bonding is $-1.1 \pm 0.3 \text{ kcal mole}^{-1}$.

This procedure was then checked on several systems where the constant contribution can be determined independently. The procedure is invaluable for incorporating into the E and C scheme systems in which there is intramolecular association. It also has the potential of extending this treatment to dimers which must be dissociated to form adducts and whose enthalpy of dissociation is unknown. Displacement reactions also fall in the category of reactions containing a constant contribution to the enthalpy.

Recently a model (called the elimination of solvation procedure) has been proposed⁴ for estimating solvation contributions to enthalpy data in weakly basic, nonpolar and weakly polar solvents. The initial tests⁴⁻⁶ on this model, although encouraging, were inconclusive because the range of solvent polarity was very limited. In this investigation, the model was put to a very rigorous test in which the range of solvent polarity was extended to include the very polar solvent nitrobenzene. Furthermore, the strong, hydrogen-bonding acid 1,1,1,3,3,3-hexafluoro-2-propanol was employed along with an expanded range of Lewis bases. The data collected also permitted a test of a solvent transfer model proposed by Christian, *et al.*⁷ After putting both models through the very rigorous tests, it was found that the elimination of solvation procedure model consistently predicted the correct results while Christian's model was less successful.

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Research such as that introduced by the above heading is normally hailed by the terminology of *magnetic exchange*. While commonly used as an indication that the exchange interactions are detected by techniques which measure *magnetic* properties, this notation leads one astray from the source of these interactions, which is indeed *electronic*. The electron spin states of two metal ions perturb each other and lead to dimer states which have an energy distribution characteristic of the magnitude of this perturbation. This distribution can be studied by various techniques such as magnetic susceptibility and epr, which measure the properties of electron *spins*. When referring to *exchange* coupling, the magnitude of the perturbation is parameterized by a value, J , and this arises from *orbital* interactions between the ions. The J value may be expressed in terms of coulomb and exchange integrals of the operator e^2/r_{ij} , and of overlap integrals between the various orbitals of the metal ions and the bridging groups.

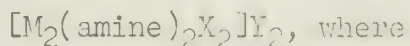
It should be stated immediately that the detailed mechanism of exchange interactions is not understood, nor is it likely to be understood in the near future. Such a level of comprehension implying the ability to predict or calculate J values: it would clearly be necessary to possess an understanding of bonding and orbital properties much more complete than today's state-of-the-art, particularly when dealing with large systems.

Why then would one want to undertake a study of magnetic exchange? First and primarily because the effects observed are intriguing and the qualitative information that may potentially be gained about the bonding in a given system is unique to this method of study. Secondly, one might consider that there are at least three general areas of vital chemical endeavor which owe their most interesting if not most important qualities to the presence of bridged metal clusters. Biochemical systems are known in many instances to involve more than one metal ion in the active site. In heterogeneous catalysis reactions of molecules on a, say, metal-oxide surface have been studied as a function of magnetic properties and the positive correlation between these phenomena and the observed reaction rates points out the possible importance of site-to-site electron exchange in the reaction sequence. Exchange coupling is certainly involved in the kinetics of solution redox reactions. The role of bridging groups in the processes of inner-sphere and outer-sphere electron transfer is of great importance and it is clear that knowledge of exchange interactions and metal-metal exchange rates is fundamental to the understanding of this field.

The generalized study of magnetic exchange for a series of metal ion systems may be conducted in several stages. The *first* of these, and often the most time consuming, is the preparation and determination of the structure of all materials. In view of the potentially large effects of small distance and angle changes, X-ray techniques should be used; or at the least a careful spectroscopic comparison should be made between each unknown system and a closely related one whose structure is precisely known. Secondly, the magnetic susceptibility and epr spectra of each material may be investigated, and all observed properties related to the electronic structure of the compounds, i.e. J values determined and any property of the data inconsistent with the quantum mechanical models should be investigated. The *third* step is to correlate J with the structural properties of each individual compound and most profitably with those for a series of related systems. This level is largely empirical

in nature - allowing future predictions of structure based upon observed magnetic data. It is the *fourth* level that requires most often the molecular insight of the researcher. That is to say that here we seek an understanding of how exchange occurs and why it displays the observed trends. In the absence of detailed information about the molecular orbitals of a system, it is the researcher's qualitative judgement which arises here, and in general can lead to many possible interpretations of the same information. It is the collection of more and more empirical data that will cause a sorting of possible interpretations, and will in the future, with the simultaneous development of quantitative techniques lead to the *fifth* level, scientific Nirvana.

The particular study reported here involves the investigation of compounds with the following formula:



M = Co(II), Ni(II), Cu(II),

amine - a tetradentate or tridentate ligand, examples:

tren = 2,2',2'' traminotriethylamine

trien = triethylenetetramine

dien = diethylenetriamine,

X = bridging group = oxalate/2, squarate/2, N_3^- , CN^- , OCN^- , SCN^- , $SeCN^-$, Cl^- , and
Y = counterion, most generally ClO_4^- or BPh_4^- .

In order to supplement the battery of spectroscopic studies, three crystal structure determinations were carried out, those of $[Ni_2(\text{tren})_2(\text{NCO})_2](BPh_4)_2$, $[Cu_2(\text{tren})_2(\text{NCO})_2](BPh_4)_2$ and $[Cu_2(\text{tren})_2(Cl)_2](BPh_4)_2$. Magnetic susceptibility and epr studies were carried out and all systems were characterized with respect to their exchange parameters. Level three results consist of the correlation of the observed J values with many properties, as listed below:

1. For linearly bridged dimers, $M-(ABC)_2-M$, J was correlated with the identity of the atoms and angular geometry of the bridge.
2. Investigations were made into the dependence of exchange on the distortion of the single ion stereochemistry.
3. J was measured as a function of extension of the bridge.
4. The electronic configuration of the metal was studied with regard to the inherent exchange properties.
5. Exchange through hydrogen bonds was detected and J was determined as a function of temperature.
6. The effect of isotopic substitution of bridge atoms was investigated.

Level four discussion of the results of this study has centered on the following considerations:

1. The orientational and distance dependence of overlap between the metal and bridge orbitals.
2. Symmetry considerations - i.e. the correspondence of the bridge orbitals used for metal bonding on one side of the bridge to those on the other.
3. Sigma *versus* pi exchange mechanisms.
4. Overlap properties of MO's within the bridge.
5. Relative energies of metal and bridge orbitals.
6. Volume of the bridging MO's.

In many cases fairly unambiguous interpretations of the observed effects have been made and in some instances it may be desirable to follow these up with single crystal epr spectroscopy to more fully characterize the single-ion *orbital* properties.

It is hoped that in the future more concrete mechanistic decisions may be made on the basis of the data obtained through this study than are currently possible.

POLY(1-PYRAZOLYL)BORATE COMPLEXES AND ORGANOMETALLICS

Robert Mink

May 7, 1974

Introduction

A relatively new class of chelating agents consisting of boron and pyrazole derivatives, first developed by Trofimenko, is now becoming the basis of an interesting research area in organometallic chemistry. These ligands can be complexed to transition metals, either in a bidentate or tridentate fashion. Depending on how they are complexed, their structures show different stereochemical nonrigidity as indicated by NMR spectra. Organometallic complexes involving the pyrazolyl borate ligands are predominantly found with the metal in an 18 electron configuration.

Complexes

The main classes of the boron pyrazole derivatives are the pyrazaboles and the poly(1-pyrazolyl)borates. The pyrazaboles^{1,2} are non-dissociable dimers of 1-boryl pyrazoles. The six-membered ring BN_4B is in a boat,³ rather than planar conformation. NMR spectra show the equivalence of the 1,3,5,7 positions as well as the 2,6 positions. These compounds are very stable, being unaffected by air and water and can be stored for years without any apparent deterioration. When a BR_2 group in pyrazabole is substituted by a transition metal, the resulting class of compounds are the poly(1-pyrazolyl)borates.⁴ These chelating ligands are uninegative and can be either bidentate or tridentate, depending on the number of pyrazolyl groups.

The bidentate $\text{M}[\text{H}_2\text{B}(\text{pz})_2]_2$ complexes can form a square planar or tetrahedral configuration about the metal.^{5,6} A planar array of nitrogen atoms about the metal with the BN_4B in a boat conformation means that the molecule can exist in two forms: a boat form with both borons up and a chair form with one up and one down.⁷ The $\text{M}[\text{B}(\text{pz})_3]_2$ and $\text{B}(\text{pz})_4^-$ ligands in $\text{M}[\text{HB}(\text{pz})_3]_2$ and $\text{M}[\text{B}(\text{pz})_4]_2$ are tridentate and give rise to distorted octahedral complexes.^{7,8}

Octahedral transition metal complexes with the configurations d^4 - d^7 can exist in two different electronic ground states, high spin and low spin, depending upon the strength of the ligand field. If, at a field strength Δ (octahedral splitting parameter) close to π (mean spin pairing energy), the separation of the two states of different multiplicity attains values within the thermally accessible range, equilibria between these states are expected to occur. This is the case for some Iron(III) poly(1-pyrazolyl)borates.^{9,10} Depending upon the substitution on the pyrazolyl rings, fully high spin, fully low spin, and complexes of intermediate spin can be produced. Solution data and solid state data for a given complex at a given temperature will differ since, in the solid state, an additional component due to packing in the lattice increases the crystal field, thus favoring the low spin state in the solid.¹¹ Therefore, a complex at a given temperature can exhibit high spin-low spin equilibria in solution, but be diamagnetic in the solid state. A change in the crystal structure is expected in going from high spin to low spin.

The discovery of the poly(1-pyrazolyl)borate anions has opened up a new area of organometallic chemistry. The tris(1-pyrazolyl)-borate ligand, $\text{RB}(\text{pz})_3^-$, forms numerous half sandwich complexes¹¹ similar to the cyclopentadienide ion. However, the tris (1-pyrazolyl)-borate complexes appear to be more stable, both chemically and thermally, than their C_5H_5^- analogs. One can change the electronic and steric effects without changing the symmetry of the molecule by substitution on the pyrazolyl rings. Trofimenko has synthesized bidentate (1-pyrazolyl)borato π allyl dicarbonyl molybdenum complexes.^{12,13} These were assumed to be 16 electron systems. There were two distinct classes, depending on whether the ligand contained alkyl or aryl groups on boron or in the 3,5 positions of the pyrazole ring. When the substitution occurs in the pyrazole ring, the complexes are very stable and do not react with nucleophiles. However, when substitution occurs at the boron, the complexes resemble an electron-deficient structure by reacting with nucleophiles to achieve an 18 electron configuration. The difference in reactivities for the two classes can be explained on steric grounds. X-ray crystallography has shown that B-H-Mo^{14} and C-H-Mo^{15} 3 center, 2 electron bonds are involved.

NMR

The temperature dependent NMR spectra of poly(1-pyrazolyl)-borate transition metal complexes indicate different types of stereochemical nonrigidity, depending on whether the ligand is complexed in a tridentate, bidentate with a B-M-Metal interaction, or just simply a bidentate fashion. When the ligand is complexed in a tridentate fashion, the mechanism involves an internal rotation of the $\text{RB}(\text{pz})_3^-$ group around the boron-metal axis.¹⁰⁻¹⁸ Attachment of bulky groups to the metal as well as substitution in the 3,5 positions of the pyrazolyl ring leads to a substantial increase in the rotational barrier. For the bidentate ligands complexed to the transition metal, the IR and NMR indicate the presence of conformational isomers.^{19,20} In solution, these conformers interconvert via ring flip mechanism. This mechanism also explains the fluxional character of some boron-substituted pyrazaboles. For bidentate ligands with a boron-hydrogen-metal interaction, IR spectra show that only one BN_2M conformation exists in solution. The crystal structures show a pair of enantiomorphic molecules in the asymmetric unit.¹⁴ In solution, the enantiomeric forms can interconvert, probably by a rotation of the pyrazolyl borate group around the metal.^{13,21}

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HYDRIDE AND ALKYL DERIVATIVES OF NICKEL

Alex N. Williamson

May 2, 1974

Recently, nickel hydrides and σ -alkyls have received much attention in the area of homogeneous catalysis. Processes such as hydrosilation, hydroformylation, isomerization, and oligomerization have been postulated to involve nickel hydrides and alkyls as intermediates. In order to obtain a better understanding of the chemistry involved, much work has been done in the areas of synthesis and characterization of these compounds.^{1,2} Today's seminar will deal mainly with these areas and, where possible, speculation will be made about the stability of these compounds.

NICKEL HYDRIDES

The first real evidence for nickel hydrides was reported by Green and co-workers in 1959.³ A high field NMR signal was observed, but a compound could not be isolated, and it was ten years later before a hydridonickel species was isolated and characterized. Today, there are over twenty-five examples of these species. They offer a wide variety of stereochemistries ranging from four coordinate trans planar⁴ to five coordinate square pyramidal.⁵ Most compounds are monomeric with terminal hydrides; however, there are examples of dimeric species with bridging hydrides.^{1,6}

Methods for preparing hydridonickel complexes can be divided into three categories: (1) those prepared by beta elimination⁷ of σ -bonded nickel alkyls to give nickel hydrides and olefins; (2) those prepared by use of hydride transfer reagents^{1,4,6,8} such as sodium borohydride and lithium borohydride, and (3) those prepared by oxidative addition of Bronsted acids to nickel (0) compounds.^{5,9,10} Of all hydridonickel species studied, only the five coordinate hydridonickel phosphites are reported to show catalytic activity. These complexes are reported to catalyze both isomerization¹¹ and oligomerization⁵ of olefins.

NICKEL ALKYLs

Alkyl nickel derivatives were originally thought to be too unstable for isolation.¹² Several of these compounds, however, do show remarkable stability to both air oxidation and hydrolysis.¹³ Compounds have been prepared by use of aluminum,^{1,14,15,16} lithium,^{17,18} and magnesium^{13,19} alkyl reagents and also by oxidative addition.¹⁶ A wide variety of stereochemistries are observed for these compounds, as we have also noted for the hydridonickel species. The geometries range from three and four coordinate planar,^{19,20} to five coordinate with 3,2 stereochemistry.² The five coordinate compounds, with the exception of the methyl derivative, decompose in the solid state almost exclusively by beta elimination.²¹ Planar mono- and dimethyl complexes react with phosphines, olefins and molecular nitrogen to form nickel (0) and nickel (1) compounds.

Structural characterizations of hydridonickel and σ -bonded alkyls have utilized primarily infrared and nuclear magnetic resonance spectroscopy. However, there are at least three examples of crystal structures. Isolation of these species seems to require the presence of π acceptor type ligands, in that all compound isolated, contained either phosphines, phosphites or olefins. Common reactivity patterns and aerial decomposition products are yet to be established for these species. Since the field is yet in its infancy, much work remains to be done.

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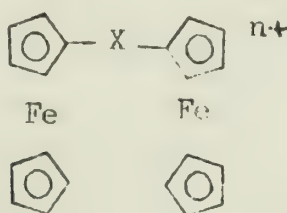
William H. Morrison, Jr.

June 27, 1974

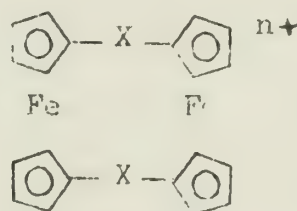
Mixed-valence compounds are those which contain the same element in formally two different oxidation states. The properties of these compounds are rarely just the sum of the properties of the two metal ions taken separately because of the interaction between the two metal centers in the molecule. The properties of mixed-valence compounds will depend upon the amount of delocalization of the valence electrons, and thus on the extent of interaction between the two moieties.

Mixed-valence compounds have received a great deal of attention lately for several reasons: 1) the close analogy between mixed-valence compounds and inner- and outer-sphere complexes formed during electron transfer reactions; 2) increased interest in understanding biological mixed-valence compounds, most notably the ferredoxin systems; 3) interest in making high temperature superconducting solids and good semiconducting materials; 4) and finally one can learn a great deal about electronic structure by studying mixed-valence compounds.

We have been interested in organometallic mixed-valence systems of the type



I



II

These compounds were chosen because: 1) they are readily adaptable to structural change, i.e. one can modify 'x', or bridge one or both rings. By doing this, the effect of metal-metal distance and ring conjugation can be studied; 2) iron is known to have several easily accessible oxidation states, and ferrocene in particular is known to be easily oxidized; 3) iron is the important biological atom; 4) a lot is known about the electronic structure of ferrocene and ferricenium.

When biferrocene (I, $x=0$) is oxidized to the monooxidized form ($n=1$), it exhibits in its electronic spectrum a feature in the near ir not found in the parent molecule ($n=0$), or in the dioxidized molecule ($n=2$). Similarly biferrocenyl (II, $x=0$), shows a feature in its monooxidized form, not found in the parent ferrocene or in the dioxidized form. These features have been assigned to the IT (mixed-valence or intervalence transfer absorption, transition in these molecules. A variety of physical measurements (Mössbauer, esr, magnetism, ir, and photoelectron spectroscopy) have shown that biferricenium⁺ has trapped or localized valences, while biferricenyl cation⁺ has average or delocalized valences.

Fitting of the physical properties to a crystal field model gives an indication as to why this is the case. There appears to be a ground state change in going from biferricenium⁺ to biferricenylum⁺. In biferricenylum⁺ the electrons are much more delocalized due to either direct or superexchange. The dioxidized forms of these molecules strongly emphasize this, with biferricenium⁺² having a susceptibility curve similar to ferricenium, while biferricenylum⁺² is diamagnetic.

Some (1.1) ferrocenophanes (II, x=CH₂, CHCH₃) have also been investigated. No band readably assignable to an IT transition was found in the monooxidized form of these compounds. The magnetism and esr properties are similar to ferricenium systems, but the Mössbauer shows anomalies which are at present not completely understood. The dioxidized form of the 1,12 dimethyl (1.1) ferrocenophane (II, x=CHCH₃) is diamagnetic, and has a Mössbauer spectrum similar to biferricenylum⁺².

STRUCTURE AND REACTIVITY OF SOME UNSATURATED
ORGANOLITHIUM COMPOUNDS

Michael R. Walczak

June 28, 1974

Organolithium compounds, such as n-butyllithium, are useful reagents for many reactions, including anionic polymerization reactions. Complexes containing an amine-solvated lithium cation coordinated to a π delocalized carbanion form an especially important class of organolithium compounds in this chemistry. Based on nmr and x-ray structural studies of these unsaturated systems, a directed covalent bonding model has been proposed to explain the relative orientation of the solvated lithium atom and the π delocalized carbanion in the solid state.¹ Crystal structures of four examples of organolithium compounds--bifluorenyl bis(lithium tetramethyl ethylenediamine), stilbene bis(lithium tetramethyl ethylenediamine), stilbene bis(lithium pentamethyldiethylenetriamine), and dilithioferrocene pentamethyl diethylenetriamine--will be presented, and some oxidation-reduction reactions of the delocalized carbanion systems will be discussed.

Bifluorenyl $\text{Li}_2\text{TMEDA}_2$ consists of two Li-TMEDA moieties associated with a bifluorenyl dianion. The geometry about each lithium atom is consistent with sp^2 hybridization, with one hybrid orbital directed toward the midpoint of the C9-C9' bond in the bifluorenyl carbanion. The remaining lithium 2p orbital bridges in a π fashion between one ring carbon p_z orbital on each of the two fluorenyl rings in the bifluorenyl carbanion. Both structures containing the stilbene group contain base-solvated lithium atoms above and below the plane of the stilbene molecule. The stilbene molecule exhibits a trans configuration about the C7-C7' bond in each structure. Ferrocene Li_2PMDTA exists as a dimer in the solid state, with two lithium atoms bridging between cyclopentadienyl rings from two ferrocene moieties. There are two types of lithium atoms in the dimer--a solvated lithium atom having all three PMDTA nitrogen atoms coordinated to it, and an unsolvated lithium atom bridging between ferrocenes.

Organolithium compounds containing a π delocalized carbanion are useful in preparing aromatic hydrocarbons² and coupled products. Molecular oxygen and transition metal halides and oxides convert the dianions to the neutral hydrocarbons, while the monoanions couple to give neutral dimeric products.

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THE SYNTHESIS, STEREOCHEMISTRY, AND REACTIONS OF CO(III) COMPLEXES
WITH AMINO ALCOHOL LIGANDS

Martha S. Okamoto

July 25, 1971

Although alcohol groups are not normally considered to be good donors in metal complexes, there is substantial evidence to indicate that atypical metal-oxygen interactions occur when the alcohol group is in close proximity to a strong donor, such as an amine. In this work the Co(III) complexes of 1,3-diamino-2-propanol (2-tmOH) and 2,3-diamino-1-propanol (1-tmOH) were studied.

2-TmOH was found to coordinate predominantly as a tridentate ligand. The most readily obtained complex was trans-[Co(2-tmOH)₂]Cl. No evidence for the tris species was ever observed. The bis complex undergoes a series of reactions in acidic solution resulting in the isolation of complexes with different degrees of protonation. The stereochemistry of these complexes was determined primarily by C-13 nmr spectroscopy. 1-TmOH, on the other hand, behaves as a simple diamine and the tris complex, [Co(1-tmOH)₃]Br₃ is readily obtained.

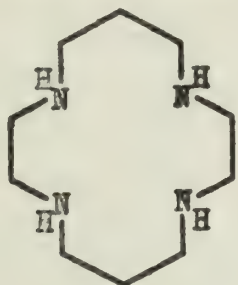
Solutions of the complexes of tmOH ligands in which a halide is coordinated and the alcohol function is dangling underwent color changes characteristic of hydrolysis reactions. It was of interest to determine whether or not the dangling hydroxyl group participated in these reactions. Coordinated and dangling hydroxyl groups are readily distinguishable by C-13 nmr. Therefore C-13 nmr studies of the base hydrolysis of cis-[Co(en)₂(NH₂CH₂CH₂OH)X]²⁺ (X = Cl⁻, Br⁻), [Co(TACN)(1-tmOH)Cl]Cl₂ (TACN = 1,4,7-triazacyclononane), and [Co(TACN)(2-tmOH)X]X₂ (X = Cl⁻, Br⁻) were undertaken.

THESIS REPORT: THE DECOMPOSITION OF NICKEL(III) COMPLEXES OF SOME MACROCYCLIC TETRAMINE LIGANDS IN BASIC SOLVENTS

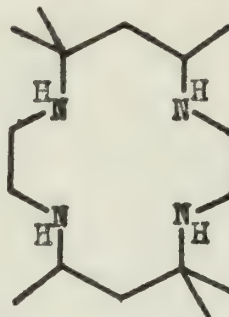
Michael T. Mocella

September 17, 1974

The nickel(III) complexes of the secondary amine macrocycles cyclam and Me₆[14]aneN₄ were found to be unstable in basic solvents



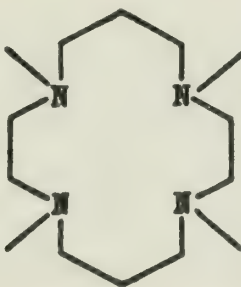
cyclam



Me₆[14]aneN₄

such as water and pyridine. However, the course of the decomposition was quite sensitive both to the particular ligand and to the solvent used. In all cases the formation of a nickel(II) ligand radical species by deprotonation of the nickel(III) complex followed by intramolecular ligand to metal electron transfer was an important initial step in the decomposition. Chemical and spectroscopic evidence in support of such an intermediate will be presented. The decomposition of this intermediate proceeded both with and without the formation of unsaturated macrocyclic complexes. The nature of these decomposition pathways has been inferred by a combination of chemical and spectroscopic methods.

The nickel(III) complex of the tertiary amine macrocycle tetramethylcyclam decomposed by different routes in water and pyridine than



tetramethylcyclam

those found for the secondary amine complexes. This was as expected, since intermediate formation as found for the secondary amine complexes is not possible in this case.

The implications of the results of this work on literature reports of metal ion-assisted ligand oxidations, metal-substrate redox processes, and the problem of the identification of the site of oxidation in metal complex oxidations, will be considered.

SYNTHETIC APPLICATIONS OF METAL VAPORS

M. D'Aniello, Jr.

November 5, 1974

The reactions of high temperature species have been studied for many years. Until about five years ago, these studies were confined to main group elements such as carbon,¹ boron,² and silicon.² More recently, attention has been focused on the transition elements. This has resulted in the development of a promising new synthetic technique for the preparation of metal-containing compounds.

The general technique involves the low pressure, low temperature co-condensation of transition metal and substrate vapors. Reaction occurs in the intimately mixed condensed phase. Such isolated metal atoms are thermodynamically activated by a large fraction of the heat of vaporization of the metal, and can undergo reactions that would normally be endothermic with respect to the bulk metal. Likewise, considerable kinetic activation is also expected. Reactions which are, at best, surface phenomena involving the bulk metal become nearly homogeneous in the condensed mixture, with the correspondingly low kinetic barriers of atom-molecule reactions. The low temperature of the mixture, however, will have a large effect on reaction rate; thus reaction may occur only after the mixture is warmed. Substrate to metal ratios are important, since reaction with substrate must occur before metal polymerization. Large substrate to metal ratios are generally employed as this increases the probability that a given metal atom will encounter a substrate molecule rather than another metal atom.

Considerable effort has gone into the design of systems in which such metal-substrate vapor reactions may be carried out. Several systems have been designed. These differ in the method of vaporization of the metal and the way metal vapor is brought into contact with the substrate on a cold surface. Systems thus far developed employ resistively heated crucibles,² electron guns,^{2,3} and even lasers⁴ to produce metal vapor. Both fixed² and rotating^{3,5} vessels have been employed to bring metal and substrate together.

A variety of complexes have been prepared using the metal vapor technique. Chromium,⁶ molybdenum,⁷ and tungsten⁷ have been co-condensed with various arenes, yielding the corresponding bis-arene complexes. Good yields can be obtained for the known bis-benzene and bis-toluene complexes. Several new complexes have been prepared involving arenes with electron-withdrawing substituents, e.g., Ph-F, Ph-OMe, Ph-NMe₂. Rates of formation vary from 1-2g./hr. to 0.1-0.2g./hr., depending on the ease of vaporization of the metal being used.

Good results have also been obtained with olefins. The new complexes Fe(1,5-cyclooctadiene)₂,⁵ Ni(1,3-butadiene)₂,⁹ and M(1,3-butadiene)₃,¹² M=Mo, W, have been prepared by the metal vapor technique. The molybdenum and tungsten complexes may very well open new fields of low-valent chemistry for these elements. Almost all the known low-valent chemistry of these elements require the presence of carbon monoxide as a stabilizing ligand. It is notable that the 1,3-butadiene complexes are stable solids, and were prepared at the rate of 0.2-0.3g./hr.

Trifluorophosphine complexes are also readily prepared by this new technique. Conventional preparations of these complexes involve long high pressure or photochemical reactions. Using the metal vapor technique, 5-10g. quantities of the trifluorophosphine complexes of most of the first row metals can be prepared¹⁰ in a few hours. Similarly, new mixed PF_3 /arene, PF_3 /olefin, and PF_3 /nitrosyl complexes have been prepared with ease.^{4,6,8,10,11}

Metal vapors can also be used to accomplish substrate transformations without necessarily isolating a metal complex. For example, a new procedure¹³ for preparing diboron tetrachloride from boron trichloride involves the use of copper atoms as dechlorinating agents. Co-condensation of copper atoms and BCl_3 results in good yields of B_2Cl_4 in up to 10g./hr. quantities. Older methods require electrical discharges through BCl_3 , with rates of formation being less than 1g./hr.

Hydrocarbon transformations have also been observed. Iron^{11,14} and nickel⁹ atoms cause cyclohexadiene to disproportionate. Chromium⁶ and nickel⁹ atoms will trimerize acetylenes to alkyl benzenes, and isomerize olefins. There are reports of ill-defined reactions between olefins and several other metals, among them aluminum,¹⁵ magnesium,¹⁶ and platinum.¹⁷

The variety of complexes prepared and uses employed thus far demonstrate that the metal vapor technique has considerable utility. Using this method, isolable quantities of compounds can be obtained, which by conventional techniques require rigorous conditions and considerable work-up time. The relatively short reaction times and, in particular, the cleanliness of reactions, recommend the technique for difficult syntheses and a basic research tool for preparation of new complexes unattainable by conventional routes.

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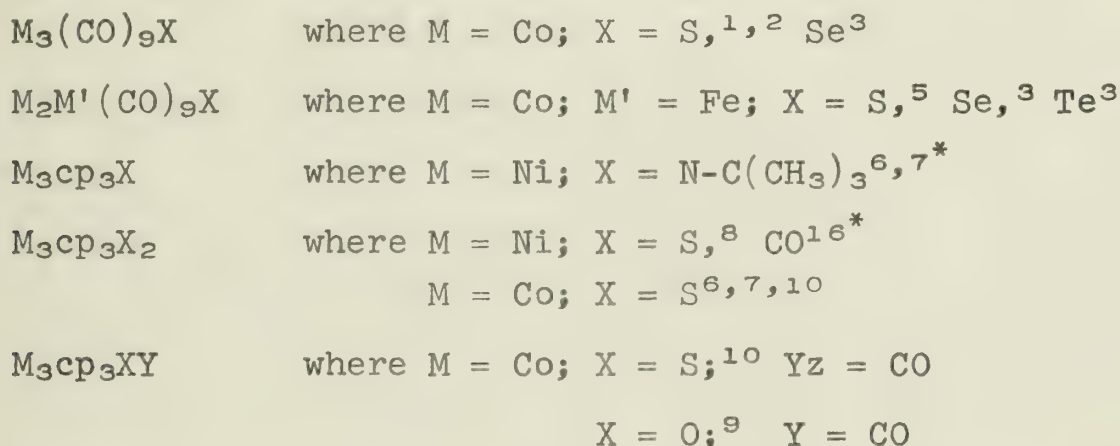
ORGANOMETALLIC CHALCOGEN CLUSTERS

David J. Kitko

December 3, 1974

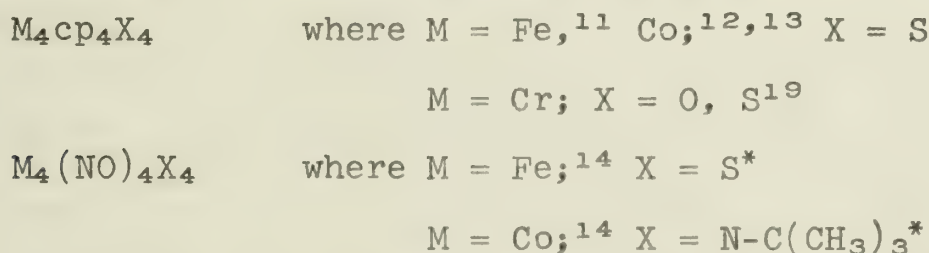
In recent years, a large number of organometallic compounds have been prepared which contain two or more metal atoms in the same molecule. An important class of these compounds are the organometallic chalcogen clusters.¹⁻¹⁹ These compounds contain a group VIA element as a bridging atom. A large number of these compounds have been prepared and characterized by Dahl and co-workers.^{2-4,8-15} They have also developed a qualitative model for explaining the metal-metal interactions through an LCAO-MO approach.^{2,3}

The trinuclear and tetranuclear chalcogen clusters of Fe, Co, and Ni are perhaps the most thoroughly studied of these compounds and will form the basis for this presentation. The trinuclear clusters prepared to date fall into two subclasses; those containing CO as the organic ligand and those containing a pentahapto-cyclopentadienyl group. The general molecular formulas are:



All these trinuclear species contain a triangular array of metal atoms with the chalcogen acting as a triply bridging group above and/or below the plane of metal atoms.

The tetranuclear species have the general molecular formulas:



In these tetranuclear species, the chalcogen atoms are again triply bridging and the metal atoms are arranged in a tetrahedral array yielding a cubane-like cluster. Distortions from a purely tetrahedral arrangement of metal atoms have also been observed in these clusters.¹¹

* Not an organometallic chalcogen cluster.

The syntheses of these cluster compounds do not follow any simple trends. A variety of extended, high temperature, high pressure reactions have been used, and the compounds are often isolated in low yields. The starting materials are usually an easily obtainable organometallic species ($\text{Co}_2(\text{CO})_8$, $\text{Fe}(\text{CO})_5$, $(\text{cpNiCO})_2$, etc.) and a chalcogen source (H_2S , S , H_2Se , or organic sulfur containing species). The clusters have reasonable solubility in organic solvents and are often separated from unreacted starting materials and undesirable by-products via column chromatography. An unusually large number of these compounds are air stable. Their characterization has involved the use of almost all available physical methods from the determination of their molecular weights via the molecular ion peak in their mass spectrum to the determination of their molecular structure via X-ray crystallography.

The extensive structural analysis of these complexes has spurred the development of the "metal cluster model"^{2,3} for treating the metal-metal bonding interactions. This model proposed by Dahl and co-workers utilizes all the metal 4s, 4p, 3d orbitals to generate a set of metal symmetry orbitals. The available ligand orbitals are used to generate a set of ligand symmetry orbitals. Those orbitals with the correct symmetry and best overlap are combined to form the metal-ligand bonding and anti-bonding molecular orbitals. A perfect pairing approximation is assumed such that the metal-ligand interactions can be separated from the metal-metal interactions. The remaining metal symmetry orbitals are combined to generate the metal-metal bonding and anti-bonding molecular orbitals. The relative energy level ordering is defined by overlap considerations and nodal character. The net metal-metal interactions are thus determined by the number of electrons which must be accommodated in these orbitals. Almost the complete range of interactions from totally bonding clusters⁹ to those with no net metal-metal bonds¹³ have been observed.

This simplified treatment is not valid for a rigorous quantitative description of the electronic structure of these molecules. It nevertheless appears to explain the existing stereochemical data (i.e., metal-metal distances and geometrical distortions). It should be noted that complications arise in this method when strong π -accepting ligands such as NO and CO are present, however, these can be accommodated.^{14,15}

A number of these clusters possess interesting chemical and physical properties. $\text{Co}_3(\text{CO})_9\text{S}$ is a paramagnetic, air sensitive compound, and an ESR study of it in solution and doped into single crystals of the diamagnetic host $\text{FeCo}_2(\text{CO})_9\text{S}$ has shown that the unpaired electron is in a non-degenerate molecular orbital of a_2 symmetry comprised primarily of an anti-bonding combination of d orbitals in the plane of the Co atoms.² $\text{Co}_3\text{cp}_3\text{S}_2$ is an air stable compound which exhibits a change in spin state from triplet to singlet as the temperature is lowered to below 195°K.¹⁷ It is readily oxidized by I_2 to yield a cationic cluster which is a simple paramagnet. The crystal structure of this cationic complex indicates that the cluster has undergone a distortion to C_{2v} geometry which is predicted by the metal cluster MO model and Jahn-Teller arguments.¹⁰ The tetranuclear cluster $\text{Fe}_4\text{cp}_4\text{S}_4$ has a distorted D_{2d} geometry. This cluster

exhibits stability in a series of oxidation states from 3 to -1 and characterization of the charged species is presently in progress.¹⁸

The organometallic chalcogen clusters are an interesting series of compounds which have provided valuable information concerning intramolecular metal-metal interactions. There are extensive efforts underway to synthesize and characterize new organometallic chalcogen complexes as well as other metal cluster compounds. These investigations will further illuminate these intramolecular interactions and perhaps help to determine their influence on the chemical reactivity of these compounds.

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THE CHARACTERIZATION OF THE 2p X-RAY PHOTOELECTRON SPECTRA
OF FIRST ROW TRANSITION METAL ELEMENT COMPOUNDS

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The x-ray photoelectron spectra of the 2p shell of transition metal halides, pseudohalides, cyanides, and other complexes are studied. The data, together with literature data, are compiled to give an overall view of the phenomenon of satellite structure.

The effects of varying the ligand, the central metal atom, and the charge on the central metal atom are analyzed.

The data are explained on the basis of a charge transfer model where a ligand $\sigma(e_g)$ electron is transferred into a metal $3d(e_g)$ orbital. This corresponds to a $\sigma(e_g) \rightarrow \sigma^*(e_g)$ or $2e_g \rightarrow 3e_g$ transition in molecular orbital terminology.

The intensities of the satellites were found to be dependent upon the type of ligand and upon the energy spacing between the two e_g sets.

A discussion of d^0 systems is included with some spectral data from compounds of second and third row transition metal elements and lanthanides.

MULTIPLE-QUANTUM ABSORPTION SPECTROSCOPY

Ronald G. Wollmann

February 11, 1975

Introduction

Multiple-quantum absorptions have been observed for many years in spectroscopic techniques spanning the energy range from high energy particle production¹ to electronic transitions² to electron paramagnetic resonance.³ These processes involve the simultaneous absorption of two or more quanta. The transitions are completely allowed and do not arise from violations of single-quantum absorption rules. Little experimental work has been directed toward the use of multiple-quantum absorptions on an analytic scale comparable to that of single-quantum absorption spectroscopic methods. This is an unfortunate situation since a multiple-quantum absorption experiment is capable of yielding information about excited states of molecules which is unattainable from single-quantum absorption experiments.⁴ The use of multiple-quantum absorption has even been proposed as a technique for isotopic separation by selectively controlling isotopic chemical reactions.⁵

Theoretical

Time-dependent perturbation theory⁶ is the basis of theoretical treatments of the interaction of electromagnetic radiation with matter. In 1931, Maria Göppert-Mayer⁷ presented the first quantum mechanical treatment of the absorption or emission of two photons. In general, time-dependent perturbation theory will yield terms to j^{th} order which describe the absorption or emission of multiple quanta. Transition probabilities from these j^{th} order terms can be obtained which describe the transition from the initial state n to the final state m . For example, the first and second order transition probabilities are

$$P_{n \rightarrow m}^{(1)}(t) \propto I(\omega) \left| \langle m | \hat{H}' | n \rangle \right|^2 g(\omega)$$

$$P_{n \rightarrow m}^{(2)}(t) \propto I(\omega_1) I(\omega_2) \left| \langle m | \hat{H}' | k' \rangle \right|^2 \left| \langle k' | \hat{H}' | n \rangle \right|^2 g(\omega_1, \omega_2)$$

where $I(\omega)$ is the intensity of the incident radiation, $g(\omega)$ is a function of the frequency which contains the time-dependence of the perturbation and affects the lineshape of the transition, and \hat{H}' is the spatial dependence of the perturbation. As can be seen from $P_{n \rightarrow m}^{(2)}(t)$, the intensity of the two-quantum absorption depends on the square of the incident radiation intensity for $\omega_1 = \omega_2$ and will be non-zero provided the matrix elements are non-zero. This gives rise to selection rules which are different than those for a single-quantum absorption. For example, $g \leftrightarrow g$ and $u \leftrightarrow u$ two-photon absorptions in centrosymmetric molecules together with polarization studies can be used to probe the excited states of molecules which can not be observed by single-photon absorption experiments.⁸

Experimental Use

Multiple-quantum absorption experiments in the optical region of the spectrum have generally been used to verify predictions made by the band theory of metals, insulators, and semiconductors.² Only recently has this technique been extended to the study of organic molecules.⁹ One-,¹⁰ two-, three-, and four-¹¹ photon absorptions have been observed in naphthalene and together with theoretical calculations¹² can be used to assign the $^1B_{1g} \leftarrow ^1A_g$ and $^1A_g \leftarrow ^1A_g$ transitions. No transition metal complex has been studied by two-photon absorption in the optical region of the spectrum; but a two-photon absorption process has been indicated in the recently investigated dipyrindinium pentachlorothallium(III) molecule.¹³ It was asserted that the process involved the initial absorption of two photons by the pyridinium ion followed by radiationless transitions to a Tl(III) resonance state from which fluorescence was experimentally observed.

Among the first multiple-quantum absorptions observed in electron paramagnetic resonance were those involving atoms such as oxygen¹⁴ and chlorine.¹⁵ More recently, multiple-quantum absorptions have been observed in sulfur¹⁶ and fluorine.¹⁷ Transition metal ions in octahedral symmetry have yielded easily interpretable multiple-quantum transitions.^{18,19} Theoretical equations have been derived to calculate the resonant field of double-quantum absorptions and to calculate the zero-field splitting in the triplet states of organic molecules.²⁰ Although these equations were derived to explain the observed spectra of organic molecules, they have been successfully applied to transition metal complexes in triplet states.^{3,21,22} The narrow linewidth of the double-quantum transition in a binuclear copper(II) complex enabled the accurate calculation of the zero-field splitting which otherwise would not have been possible with any degree of accuracy.²¹

Summary

Multiple-quantum absorptions have been observed by many spectroscopic techniques for many years. Chemists have just begun to recognize that useful information can be obtained from these processes. With the refinement of experimental techniques in the optical region of the spectrum, experiments with transition metal complexes will undoubtedly become possible. Extension to states other than triplet states should also occur in the near future in electron paramagnetic resonance experiments.

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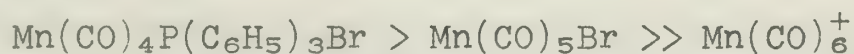
KINETICS AND MECHANISMS OF METAL CARBONYL REACTIONS

Jim Atwood

Final Seminar

February 25, 1975

One major area of study has been $M(CO)_5Br$ where M is Mn or Re and derivatives of these compounds. $Mn(CO)_5Br$ and $Re(CO)_5Br$ have both been studied with ^{13}CO exchange and $P(C_6H_5)_3$ substitution kinetics. The reactions take place by a rate determining dissociation of radial CO, leading to a five-coordinate intermediate which is fluxional, and which rapidly picks up a ligand to reform the six-coordinate species. $Cis\ Mn(CO)_4P(C_6H_5)_3Br$ has also been studied and shows a cis labilization by the $P(C_6H_5)_3$. In $cis\ Mn(CO)_4P(C_6H_5)_3Br$, CO dissociates from one of the two positions cis to both Br and $P(C_6H_5)_3$, at a rate which is five fold greater than the rate of dissociation from $Mn(CO)_5Br$. The five-coordinate intermediate can be shown to be fluxional as well. These data suggest a previously unnoticed cis activation by weaker π -bonding ligands. Coupled with data on the $Mn(CO)_6^+$, we have the following sequence for dissociation from manganese carbonyls:



Interpreting metal carbonyl reactions from the literature shows cis labilization to be a very general phenomenon and leads to the following ordering for cis labilization by ligands



This is the reverse of the "trans effect" order.

Cis labilization has many applications to reactivity of low valent metal complexes. In addition to the obvious applications to octahedral metal carbonyl reactions, there are possible applications to metal carbonyl cluster reactions and catalytic hydrogenations that proceed by oxidative-addition of H_2 to square planar complexes.

The second major area of study has been the kinetics of substitution and exchange of $Co_2(CO)_8$. This molecule has obvious importance because of its catalytic properties, but kinetics studies have been complicated by the rapidity of its reactions. I have studied the kinetics of exchange with ^{13}CO at $0^\circ C$. and have found a significant rate dependence on the concentration of ^{13}CO . Observation of this unusual dependence on the ^{13}CO concentration led to a study of the kinetics of $Co_2(CO)_8$ reaction with other ligands such as $P(C_6H_5)_3$. The rate of reaction of $Co_2(CO)_8$ with $P(C_6H_5)_3$ shows more than first order dependence on the concentration of $Co_2(CO)_8$ and also a dependence on the concentration of $P(C_6H_5)_3$, indicating a complicated rate expression. Work is proceeding to determine the exact form of the rate expression. It appears unlikely, however, that these reactions are proceeding by a dissociative process as previously thought.

POLYMER SUPPORTED GROUP VIII TRANSITION METAL HOMOGENEOUS
CATALYSTS

Steve Richter

February 27, 1975

Catalysts are vitally important in today's chemical process industries. The basic chemical technology used in fertilizer manufacture, petroleum refining, petrochemical manufacture, or coal and coal-tar derivative processing involves processes that depend on catalyzed reactions.¹

Historically, catalysts have been divided into two classes, namely, heterogeneous and homogeneous. In heterogeneous catalysis, a phase boundary exists between the catalyst and the reacting species (substrate). In homogeneous catalysis, all the species are in the same phase, most commonly the liquid phase.

Heterogeneous catalysts are preferred in industrial operations, mainly because of the ease of separation of the catalyst from the reaction mixture. However, they have several drawbacks, because often they are not very specific, require high temperatures and pressures for operation, only have a small portion of their active sites readily accessible, and are difficult to design and improve.²

On the other hand, homogeneous catalysts are generally highly specific and highly active, react under comparatively mild conditions, and can have the steric and electronic environment of the active site widely varied. The great disadvantage of homogeneous catalysis is the difficulty with separation of the catalyst from the product, which often makes the process economically unfeasible.² Also, self-aggregation produces inactive species at high catalyst concentrations.

Many of the problems of the two types of catalysts could be overcome if the best properties of each were combined. This combination, in effect, would be making a heterogeneous catalyst out of a homogeneous one. In recent years, much effort has been devoted to making heterogeneous catalysts by linking homogeneous transition metal catalysts to solid supports.^{3,4}

One type of solid support widely used for this purpose is an organic polymer. Most of these have been polystyrene derivatives, since polystyrene can readily be functionalized with a variety of reactive groups. In addition, since a large number of homogeneous transition metal catalysts contain phosphine ligands, the majority of these reactive groups have been phosphine derivatives.⁵

One system in which these polymer supports have been used involves Wilkinson's hydrogenation catalyst, $\text{RhCl}(\text{PPh}_3)_3$. Grubbs and coworkers⁶ have attached this homogeneous catalyst to a polystyrene support by phosphine links. The bound catalyst was easily separated from the reaction mixture by filtration and could be used many times with almost no loss in activity. A study of the rate of reduction versus size of olefin indicated that the polymer supported catalysts were selective for smaller molecules. Additional studies showed that this polymerized catalyst was regioselective in the hydrogenation of unsaturated steroids.⁷

Strukul, et al,⁸ found that polymer bound cationic Rh(I) complexes were selective hydrogenation catalysts of olefins and ketones. Changing the substituents on the phosphorus atom of the polymeric ligand changed the catalytic behavior of the metal complex.

Another system involves the hydroformylation catalyst $\text{Co}_2(\text{CO})_8$ and its phosphine substituted derivatives. Pittman and coworkers⁹ have synthesized a polymer supported catalyst similar to the phosphine substituted homogeneous $\text{Co}_2(\text{CO})_8(\text{PPh}_3)_2$. The bound complex had approximately the same activity and selectivity as its homogeneous counterpart.

It has been known for several years that Rhodium complexes, such as $\text{RhH}(\text{CO})(\text{PPh}_3)_3$, are more reactive and can be used under milder conditions for hydroformylation than the cobalt complexes. Pittman and coworkers¹⁰ have also prepared the polymer supported analog of this homogeneous catalyst. The heterogenized catalyst had roughly the same activity and selectivity as the monomeric species, but the supported catalyst also retained its activity through many recycled batch operations.

Care must be exercised, however, since the catalytic chemistry of polymer bound transition metal complexes can not always be inferred directly from that of the homogeneous analog. Side reactions can result in the formation of surface functional groups on the polymer other than those intended.¹¹ Another problem with supported catalysts, one which they share with conventional heterogeneous catalysts, involves the very difficult task of characterization of the active sites. However, new techniques are being developed in surface science which might be of use in elucidating the structure and composition of the active sites in these catalysts.¹²

Overall, polymer supported homogeneous transition metal catalysts seem to combine the best advantages of both heterogeneous and homogeneous catalysts. Some of these advantages are a) easy separation from the reaction mixture, possible regeneration, and reuse of the catalyst, b) less sensitivity of the catalyst to poisoning impurities, c) sometimes an exhibition of higher catalytic activity by the supported catalyst, and d) great versatility due to the many possible modifications which can be made on the polymer support.

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CALCULATED TRENDS IN DINITROGEN BONDING

John Gaul

March 6, 1975

Introduction

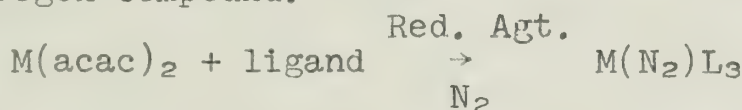
Since the discovery of $\text{Ru}(\text{NH}_3)_5\text{N}_2^{2+}$ by Allen¹ in 1965, tremendous efforts have been made to isolate and characterize new compounds containing N_2 . To date, there exists almost 200 such compounds encompassing 18 transition metals. Their oxidation states range from zero^{2,3,4} to five⁵ and can have coordination numbers in solution from three⁶ to the more common^{7,8} four and six. In addition, many bis- N_2 and N_2 bridged systems exist. Formation of these bridged systems from mononuclear N_2 compounds indicates that the reactivity of the N_2 is effected little by coordination.^{7,8} The frequency (ν_{NN}) is usually lowered to $\sim 1600\text{-}1700\text{ cm}^{-1}$ (compared to free $\text{N}_2 \sim 2331\text{ cm}^{-1}$), indicating a reduced bond order⁹ and perhaps "activation" of the N_2 .

Structure of the N_2 Moiety

Almost all N_2 compounds known today consist of linear fragments in agreement with m.o. calculations of stability.¹⁰ There are a few notable exceptions. An x-ray structure on a Ni dimer, $[(\text{C}_6\text{H}_5\text{Li})_4(\text{C}_6\text{H}_5)\text{Li}_2\text{Ni}_2\text{N}_2(\text{Et}_2\text{O})]_2$, indicates the $\text{N}=\text{N}$ bond axis is at right angles to the Ni-Ni bond.¹¹ Bercaw reports dinitrogen π bonded to a titanocene.¹² Most other edge-on bonded N_2 complexes have been found by matrix isolation techniques.

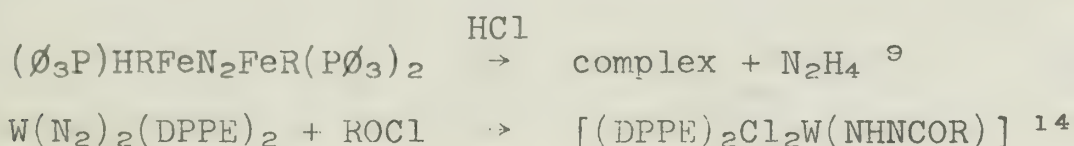
Preparations and Reactions of Coordinated N_2

Most dinitrogen compounds can be prepared in similiar fashions. Usually, the metal as an acetylacetonate is reduced (aluminum alkyl, Grignard reagent, Zn/Hg) in the presence of NH_3 or PR_3 and N_2 to yield the dinitrogen compound.^{6,7}



The ligand may be NH_3 , PR_3 , H_2O , X^- , CO , H^- , 3° arsine or a 3° stibene.

The reactions of coordinated N_2 for the most part consist of substitutions of the N_2 by CO , H_2 or some other ligand. There is, however, a growing number of N_2 -compounds that react to yield stable N-H and N-C bonds and these are generating considerable interest.^{9,14,15,16} Some examples are



M.O. Calculations

Hopes of understanding why some dinitrogen compounds seem to activate N_2 whereas others leave the N_2 little changed from free N_2 has led to theoretical calculations of varying degrees of sophistication. Insight into dinitrogen bonding is obtained from stability predictions

from simple Hückel and calculations of bond order and charge distribution from CNDO and ab initio SCF methods.

Though a simple Hückel calculation is of little value in a quantitative sense, when applied to dinitrogen compounds provides insight for predicting which metal and its appropriate oxidation state should result in greater stability.¹³ They were also able to calculate curves for electron charge and bond order as a function of δ (a term relating the energies of the π orbitals of N to the d orbitals of the metal).

These results are in accord with a subsequent calculation¹⁷ of the same quantities by a different method. However, the latter calculations are much more quantitative and broader in scope. Charges on the metal and each nitrogen were calculated along with degrees of σ to $d\pi-p\pi^*$ bonding for metals in the 1st and 2nd transition series. Some very definite trends were observed. Calculated stabilities of the M-N₂ moieties were plotted for the first two transition series in various oxidation states. Trends in bond orders were also observed.

I.R. and ESCA

Experimental verification of the m.o. calculations for Fe, Ru, Os, Ir and Re was attempted with ESCA and IR. These metals were selected for a number of reasons:

- (1) they have been studied extensively
- (2) Fe, Ru, Os are a triad and thus might show trends
- (3) Re, Os, Ir are a 5d sequence and it might be learned if the trends hold true for these metals.

Charge separation data was obtained using correlation plots of N1s binding energies vs. calculated charges for nitrogens in various formal oxidation states.^{18,19} Correlation diagrams corresponding to three calculation methods were obtained. Results with Re, Ir, and Fe seem to correspond to predicted trends whereas those for Ru and Os are inconclusive. Charge separation data calculated by another method²¹ for Ru and Os does seem to correlate. Metal core binding energies were measured for all five metals and trends in the magnitude of the positive charge tabulated.

From the ESCA studies, it is seen that the N≡N bond is quite polar²⁰ in N₂ complexes. The authors conclude that the charges in the nitrogens are opposite to the trends predicted by m.o. calculations.

IR intensity values are interpreted in terms of the relative amounts of $d\pi-p\pi^*$ bonding to σ -bonding in these compounds. The intensity to frequency^{21,23,24} plots indicate a great deal of similarity between the Fe²⁰ and Ru²⁵ complex while the predicted trend is seen for Ru and Os and for Re, Os and Ir. These IR intensities were of value in providing a check on the method of charge assignment noted above.

Thus, from experimental data (IR and ESCA), overall trends of charge separation, bond order and relative importance of $d\pi-p\pi^*$ bonding both across a series and down a triad seem to agree with calculated trends. The convention of assigning charges to the two nitrogens is seen to be disputed with conclusions arrived at experimentally.

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STUDIES ON THE FERRIC DITHIOCARBAMATE SPIN EQUILIBRIUM SYSTEM

Gretchen Hall

Final Seminar

March 11, 1975

The Fe(III) dithiocarbamates have been extensively studied,¹ however, the spin equilibrium system is still not well characterized. Iron-57 Mössbauer studies have set a lower limit on the spin flipping rate of 10^7 sec^{-1} , and this has led to the suggestion that these are mixed spin instead of spin equilibrium systems.² Our work has concentrated on establishing a qualitative estimate of the spin flipping rate and on determining the details of the electronic structure of the ferric dithiocarbamates.

Magnetic susceptibility data have been collected from 296-4.2°K for ten Fe(III) dithiocarbamates and for two Ru(III) dithiocarbamates. The ferric dithiocarbamates exhibit a Boltzmann population distribution over the three Kramers doublets from the low spin (2T_2) ground state and over the three Kramers doublets from the high spin (6A_1) excited state, however, the susceptibility data can not be fit with a simple 2T_2 - 6A_1 equilibrium model. It is necessary to include a vibrational partition coefficient³ (or a mathematically equivalent temperature dependent 2T_2 - 6A_1 energy separation) to fit the data.

Infrared measurements from ambient temperature to 30°K on these systems have been used to 1) determine the validity of using the vibrational partition coefficient, and 2) set an upper limit on the spin flipping rate. The ir data for structurally analogous cobalt, ruthenium, and manganese dithiocarbamates have been used to help in the understanding of the ir spectra of the iron systems.

Epr studies from 85-4.2°K have been made on these systems. Measurements on the completely high spin ferric dithiocarbamates and the low spin ruthenium dithiocarbamates have been used to interpret the epr work.

The ir and epr results set an upper limit of 10^{10} sec^{-1} on the spin flipping rate. The ir data also shows that the previous analysis of the susceptibility data based on either a vibrational partition coefficient or a temperature dependent energy separation is incorrect. One possible alternative is a model involving extensive vibronic interaction in the 2T_2 levels.

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AN ELECTRON SPIN RESONANCE STUDY OF SOME COBALT(II) COMPLEXES

Ben Tovrog

Final Seminar

March 18, 1975

Recent studies involving planar cobalt(II) complexes have revealed interesting reactivities with regards to adduct formation. Extensive studies on porphyrin and Schiff base systems have shown that in the presence of a coordinating Lewis base, a molecule of dioxygen will coordinate forming a six-coordinate complex. Speculations concerning the influence of the axial base and in-plane ligand set in the subsequent reaction with dioxygen have been made. ESR studies, however, which can be very useful in determining the electronic structure of these five-coordinate base adducts have been limited, likely due to the weak acidity of the cobalt center.

In addition to the specific problem state above, the general area of the influence adduct formation has on the esr of transition metal complexes is of interest. Consideration of experimental limitations, relaxation effects and known chemistry cause one to conclude that such studies can be effectively conducted only on first row $S=1/2$ low symmetry systems. It is then understandable that much work has been done in the area of copper(II) complexes, though many studies in this area have produced confusing and conflicting results. For these reasons, we have chosen to study BF_2 capped bis-diphenylglyoximecobalt(II), due to the fact that, in contrast to previously studied cobalt(II), this complex readily forms both 1:1 and 2:1 adducts with a wide variety of nitrogen and oxygen donors. Our interest in this system was further heightened by the fact that solutions of $\text{Co}(\text{DPGB})_2$ with stoichiometric amounts of added base readily form dioxygen adducts at low temperature. The coordinated dioxygen, however, can be displaced with addition of excess base, forming the 2:1 base adduct. The BF_2 capped rather than the proton bridged ligand was chosen for study due to the decreased basicity of the glyoxime oxygens which allowed study of adducts formed from weak donors, due to the decreased tendency for dimer formation.

The esr studies have been conducted both at liquid nitrogen temperature in glassy media and at room temperature in solution. All adducts are low-spin and characterized by an orbitally non-degenerate ground state, $(d^7)^1$. A crystal field treatment of the anisotropic spin-Hamiltonian g and A values has been used, with spin-orbit effects from excited states included as a perturbation. Ligand hyperfine have been similarly analyzed.

Comparing our data with that for other systems, it is noted that the cobalt center in $\text{Co}(\text{DPGB})_2$ has a larger $\langle 1/r^3 \rangle$ (higher positive charge). This result is used to explain the interesting finding of increased nitrogen and decreased phosphorus hyperfine coupling when compared to $\text{Co}(\text{salen})$ adducts of similar bases.

The wide variety of 2:1 adducts of both nitrogen and oxygen donors has revealed wide variations in the P values ($P \propto \langle 1/r^3 \rangle$) characterizing the complex, indicating that variations in axial donors can significantly alter the electronic structure. Correlations between these P values, with E_B and C_B numbers characterizing the base, exist and provide insight as to factors influencing charge distribution in these adducts. It has been found that the P value is very dependent on E_B of the axial base. C_B has obvious importance because for bases with similar E_B , P decreases in the order O donor > N donor > P,S donor.

THE EFFECTS OF METAL AND LIGAND VARIATION ON THE MASS SPECTROMETRIC FRAGMENTATION OF TRANSITION METAL COMPLEXES

Jan Collard

Final Seminar

March 25, 1975

Although mass spectrometry has been in existence for quite some time, it is only beginning to be exploited by transition metal chemists. It has been found that the fragmentation pattern of an organic ligand changes upon complexation with a metal ion.¹ This is not surprising in light of the theory of mass spectrometry which predicts that a bombarding electron in the ion source interacts with a molecule causing it to emit an electron from the highest occupied molecular orbital (HOMO).² Molecular orbital theory has shown that, in general, the HOMO of a transition metal complex is composed essentially of metal d orbital character.³ Thus, the electron that will be emitted has a large percentage of metal d character in the metal complex.

The object of this particular study was to investigate the influence of the metal d electronic configuration on the fragmentation of a transition metal complex in the mass spectrometer. To do this, a series of complexes with very similar ligands and varying metal d electronic configuration was needed. Such a series is the iron(III) dithiocarbamates of general formula $\text{Fe}(\text{S}_2\text{CNR}_2)_3$. Recently,⁴ the electronic structure of these complexes was discussed, and it was shown that the electronic state for these complexes varies with a change in the alkyl substituent R. As a control group, the cobalt and ruthenium analogs of the dithiocarbamates were also studied. The electronic configuration of these compounds remains constant throughout the series.

The fragmentation patterns of these complexes are interesting and unique and the presence of the metal ion in the compound allows one to see types of fragmentation not observed for organic compounds. Such processes can be explained utilizing a valence change concept⁵ which invokes the variability of valence state found for transition metals.

As the amount of low spin character in these complexes increases, there is expected to be a consequent increase in the strength of the metal-ligand interaction. This increase in interaction should be reflected in the mass spectra by an increase in the number and intensity of ions containing the intact metal-sulfur bond. However, there are many competing fragmentation pathways possible, making a linear correlation with metal-sulfur bond strength impossible.

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METAL COMPLEXES OF FOURTEEN-MEMBERED MACROCYCLIC LIGANDS CONTAINING TERTIARY AMINE DONORS

Frank Wagner

Final Seminar

April 15, 1975

A wide variety of macrocyclic ligands that contain some combinations of nitrogen, oxygen and sulfur donors have been synthesized and studied during the past fifteen years.¹ The majority of the macrocycles studied are fourteen-membered ring systems with nitrogen donors. Very little attention, however, has been given to macrocyclic ligands that contain tertiary amine donors.^{2,3}

Initially, a fully alkylated fourteen-membered macrocyclic complex of Ni(III) was required for redox studies.⁴ Reaction of cyclam with formic acid and formaldehyde (Eschweiler-Clarke reaction) afforded the tetramethylated derivative (TMC) in good yields. Treatment of Ni²⁺ with TMC in ethanol led to the isolation of the red, crystalline complex, NiTMC(ClO₄)₂. The complex exhibited an unusual lability in dilute mineral acids, rapidly decomposing to aqueous Ni²⁺ and protonated ligand. In addition, the ligand was completely transferred from nickel to either Cu²⁺ or Ag⁺ in aqueous solution. Such a lack of kinetic stability could not be explained in terms of the donor properties of the tertiary amine but must result from the stereochemistry of the ligand about the metal center. Of the five possible sets of nitrogen configurations, the physical and chemical properties of NiTMC²⁺ and analogous Zn²⁺ complexes suggested that all four N-methyl groups were on the same side of the molecular plane.⁵ This is not the thermodynamically favored form (Nicyclam²⁺ structure) but is a kinetically controlled product. A crystal structure determination on Ni(TMC)N₃⁺ confirmed the assignment of stereochemistry.⁶

Attempts to synthesize the thermodynamically stable form led to development of procedures for alkylating deprotonated species. Treatment of Nicyclam²⁺ with KOH in DMSO followed by addition of methyl iodide yielded a tetramethylated product quite different in properties from NiTMC²⁺. A crystal structure determination of a mono-azido bridged dimer indicated that the ligand possessed the cyclam-like stereochemistry which is the thermodynamically most stable form.⁷ The deprotonation reactions were applied to other macrocyclic systems utilizing sodium methylsulfinylmethide in DMSO as the base-solvent system. Alkylation reactions were restricted to alkyl halides without beta-hydrogens since elimination competed with substitution. Most alkylations were stereospecific, but in some cases rapid proton exchange among nitrogen sites in the deprotonated species dictated the distribution of products. Attempts to unequivocally determine the stereochemistry of a variety of alkylated products from the aforementioned reactions led to development of a new "template" synthesis of fourteen-membered macrocycles.

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INORGANIC APPLICATIONS OF RESONANCE RAMAN

David S. Bieksza

April 24, 1975

Introduction

The Raman effect is essentially a light-scattering phenomenon. A portion of the incident radiation is scattered by a molecule at altered frequency according to the molecule's characteristic energy levels. Depending on the position of these energy levels, the frequency shifts in the scattered radiation correspond to rotational, vibrational, or electronic transitions.¹ The resonance Raman effect involves the relationship of the incident radiation to the frequencies of electronic transitions in the molecule. Two separate cases may be distinguished. The pre-resonance effect occurs when the incident frequency approaches a transition frequency. In this case, the intensities of certain peaks in the Raman spectrum increase compared to the rest. The rigorous resonance case, on the other hand, occurs when the incident frequency falls within the band envelope of the transition. The enhancement of intensity is so great that overtones and occasionally combination bands appear.²

Theory

The intensity of scattered radiation for a freely rotating molecule at frequency ν_s over the entire solid angle is proportional to the intensity of the incident radiation, the fourth power of the scattered frequency (hence the " ν^4 law") and the sum of the squares of the elements of the polarizability tensor.³ However, the functional dependence of the elements of the polarizability tensor has been derived employing two different approaches. Dispersion theory, modified for resonance conditions, yields an equation which relates each element of the tensor to a sum of virtual excited electronic states, taken singly, and all the vibrational sub-levels of each state. Another derivation, through time-dependent perturbation theory,⁴ yields an equation relating each element of the polarizability tensor to a sum of virtual excited electronic states, taken pairwise. Superficially, both equations explain the enhancement of intensity in the same manner: As the incident frequency approaches the frequency of an electronic transition, the denominators of both expressions decrease, thus intensity increases. A damping constant, related to the half-width of vibrational fine structure in an electronic absorption band, prevents infinite intensity in the rigorous resonance case. The point should be made here that both summations are over virtual states only. Unlike fluorescence, the Raman effect is a light-scattering phenomenon, that is, the incident photon is not absorbed by the molecule. Instead, the molecule is perturbed so that a vibrational transition occurs.⁵

The physical meaning of these equations is that the intensities of Raman bands are governed by the relationship of the ground electronic state to the excited states. If the ground state is vibronically coupled to a single excited state, then only that state will influence the intensities of the Raman bands. Furthermore, only those vibrations mixing ground and excited states exhibit the resonance Raman effect. Likewise, if a pair of excited states are vibronically coupled, both states influence the Raman intensities. Once again,

only those vibrations mixing the two excited states exhibit the resonance Raman effect.⁶ Experimentally, these can be distinguished by a study of relative intensities as a function of exciting frequency. Mathematically, the influence of a single excited state is related to diagonal vibronic energy terms whereas the influence of two excited states is related to off-diagonal vibronic energy terms.⁷ Finally, only electronic transitions that are both spin-allowed and Laporte-allowed enjoy non-zero transition moments in the relevant equations, and so only these excited states can influence enhancement of intensities.

Experimental

The purposes of the resonance Raman technique are to study vibrations which might otherwise have weak or badly-overlapped bands, to learn more about vibronic coupling of electronic states, and (in common with non-resonance Raman) to draw conclusions on the bonding within the molecule in question. Often reports have concentrated on this last aspect. For example, extensive studies have been conducted on tetrahedral,⁸ octahedral,⁹ and square planar¹⁰ molecules incorporating halogens. From observed intensities, it was determined that only single excited states governed the intensity enhancement in Group IV tetrahalides, but pairs of excited states influenced the intensity enhancement in square-planar and octahedral anions. Information on the bonding in these complexes was obtained through the calculation of mean bond polarizability derivatives, corrected for the resonance Raman effect. Results confirmed measurements by other techniques that the covalent character of the bond gradually increases as the halogen changes from fluorine to iodine. Also, covalent character was found to increase with increasing formal charge on the metal atom in anionic complexes. Mean bond polarizability derivatives could be decomposed into parallel and perpendicular bond polarizability derivatives. In all cases, the former proved to be more sensitive to the nature of the bond. Another study¹¹ on overtones of the permanganate and chromate ions allowed an estimate of bond dissociation energy to be made, indicated environmental effects on the widths of overtones, and suggested an equation predicting the relative intensity of the overtones.

More complicated systems have generally been limited to biological molecules and their models, since resonance Raman provides a technique for monitoring vibrations of a chromophore independent of its matrix.¹² However, an investigation of tetracarbonyldi- μ -2,2,5,5-tetramethylhex-3-yne-diiron has been reported. An analysis of relative intensities and depolarization ratios indicated that promotion of electrons in the iron-iron double bond is the transition which most strongly enhances intensity. A smaller contribution arises from an iron-acetylene charge transfer transition. And, in another investigation,¹⁴ the resonance Raman spectrum of various ferricenium ions showed that only those vibrations involving the iron atom are enhanced enough to be observed. Two other bands are attributed to electronic transitions between low-lying spin-orbit states.

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ELECTRON-NUCLEAR DOUBLE RESONANCE (ENDOR) OF TRANSITION METAL COMPLEXES

Timothy R. Felthouse

May 1, 1975

Introduction

The ENDOR method was proposed by Feher in 1956, as an extension of a dynamic nuclear polarization scheme.¹ Nuclear magnetic resonances at hyperfine frequencies were detected through their concomitant effect on the electron paramagnetic resonance (EPR) signal. Applications of ENDOR to paramagnetic transition ions in diamagnetic hosts yielded nuclear g values and coupling constants for hyperfine and nuclear electric quadrupole interactions. The entire scope of materials subjected to the ENDOR technique has been diverse: paramagnetic defects in solids, organic radicals in solutions and liquid crystals, magnetically dilute metal complexes in single crystals and powders, and proteins.²⁻⁶

Theory and Experimental Approaches

An ENDOR transition corresponds to a change in the nuclear magnetic quantum number of one unit while the electronic quantum number remains fixed. Consequently, an ENDOR spectrum displays the EPR signal intensity as the nuclear radio frequency (in MHz) is swept. In order to account for the observability of an essentially nuclear transition, consideration must be made of the induced transition rates and spin populations between the electronic and nuclear levels, principal relaxation paths, and a radio frequency (rf) enhancement factor.⁷⁻⁹ Three mechanisms can be distinguished to explain the full range of ENDOR effects: steady-state ENDOR, the "packet-shifting" model, and "distant ENDOR." The mechanisms are not mutually exclusive, although no comprehensive theory of the ENDOR mechanism in solids now exists.

Four main directions have evolved by which the ENDOR experiment is performed: "low power ENDOR" in either the EPR dispersion or absorption mode, transient ENDOR, and "high power ENDOR."¹⁰ A commercially available spectrometer employs the "high power ENDOR" approach, using rf fields up to 12 gauss.¹⁰⁻¹³ The intense nuclear fields are necessary for studies on solutions or solids with short relaxation times or transition metal complexes in which the delocalized spin density onto the ligands decreases the effect of the rf enhancement factor.

Applications

Rist and Hyde have investigated the ligand ENDOR of copper(II) complexes in magnetically dilute organic single crystals and powders.¹⁴ In the single crystal work proton and nitrogen hyperfine couplings were determined as well as the nitrogen quadrupole coupling which is observed as a first-order splitting in the ENDOR spectrum. Proton resonances occur in pairs about the free proton frequency and are separated by their hyperfine interaction A, while a nitrogen ENDOR spectrum consists of four lines centered about A/2 with splitting

by the quadrupole and nuclear Zeeman interactions. A key feature which emerged out of the powder ENDOR work was that "single-crystal type" spectra could be obtained in some cases where there was a dominant magnetic interaction so that the magnetic field setting and modulation could select molecules in restricted orientations. However, single-crystal ENDOR spectra are required for the assignment of resonances and hyperfine couplings to the ligand nuclei.¹⁵ As an extension of their work on copper(II) complexes, Hyde and coworkers studied the ligand interactions in a frozen solution of the blue copper(II) protein stercyanin.¹⁶ Although the ENDOR spectrum was not well resolved, they concluded that the copper ion was in a hydrophobic environment and at least one coordinating ligand was nitrogen.

ENDOR has been quite successful in probing the various interactions in iron metalloproteins. Sands and coworkers determined the effective hyperfine tensors for the reduced two-iron ferredoxins.^{17,18} For ⁵⁷Fe enriched samples the ENDOR line frequencies corresponded to a ground state of $S = \frac{1}{2}$, supporting the model of an antiferromagnetically coupled high-spin Fe(II), Fe(III) pair. Although the first investigation of single crystals of metmyoglobin was unable to resolve the ligand hyperfine couplings,¹⁹ Feher and coworkers later found that frozen solutions enabled observation of proton, nitrogen, and ⁵⁷Fe hyperfine interactions.²⁰ Subsequently, mixed crystals of myoglobin containing about 90% of the diamagnetic CO-ligated form have yielded a preliminary report of the diagonal components of the heme nitrogen hyperfine and quadrupole tensors and the ⁵⁷Fe anisotropic hyperfine interaction.²¹ Further work on mixtures of hemoglobin and its met form hopes to monitor the cooperative oxygenation effect using ENDOR of various ligand nuclei.

Summary

Hyperfine and quadrupole interactions that are normally too small for measurement from EPR spectra can be readily determined with high accuracy by the ENDOR technique. Furthermore, EPR spectra of transition metal complexes often contain ambiguities in assignment of superhyperfine splittings, whereas ENDOR spectra provide sets of resonances from magnetically equivalent nuclei. The ENDOR studies which have been performed on bioinorganic molecules should serve as a basis for applications to synthetic analogs and a variety of coordination compounds.

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MECHANISMS OF SUBSTITUTION REACTIONS OF METAL CARBONYL HYDRIDE COMPLEXES

Blaine H. Byers

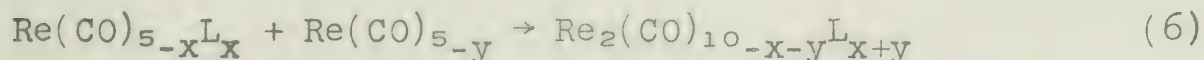
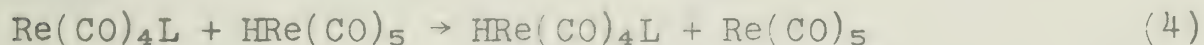
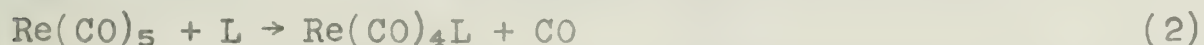
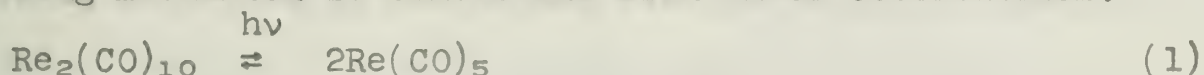
(Final Seminar)

May 6, 1975

Transition metal carbonyl hydrides of manganese and rhenium were first prepared in 1957 and 1958 respectively. Although numerous substitution and exchange reactions have been examined,^{1,2} the kinetics and mechanisms of these reactions have not been elucidated.

Several different mechanisms for substitution reactions of various metal carbonyl complexes have previously been determined: CO dissociation for $\text{XM}(\text{CO})_5$ (X = halide); associative displacement for $\text{CoNO}(\text{CO})_3$; and ligand migration for $\text{CH}_3\text{Mn}(\text{CO})_5$. The emphasis of this study has been to determine which of these mechanisms obtains for the carbonyl hydrides.

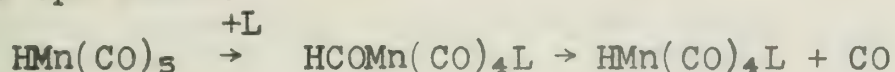
Substitution of PBu_3 for CO in $\text{HRe}(\text{CO})_5$ has been investigated. The observed kinetics cannot be explained by any of the above mechanisms. Rather, a unique radical chain process has been proposed. $\text{M}(\text{CO})_5$ radicals (M = Re, Mn), which initiate the chain reaction, are generated by monochromatic irradiation of $\text{M}_2(\text{CO})_{10}$ at the wavelength corresponding to the metal-metal $\sigma \rightarrow \sigma^*$ transition. In the absence of $\text{M}_2(\text{CO})_{10}$ or other radical initiators (including trace impurities), substitution is extremely slow in hexane at ambient temperature. The following mechanism is consistent with these observations.



Reactions (2) through (5) are chain propagating steps, while step (6) terminates the process. Polysubstituted dirhenium species are observed as the reaction proceeds, further supporting the above mechanism. Extensions of this chain process to analogous halogen systems as well as polynuclear hydrides are likely.

While attempting to clarify the above mechanism, the interaction of photochemically generated $\text{Re}(\text{CO})_5$ radicals with molecular hydrogen was observed to produce several hydride species. At low photon flux, $\text{HRe}_3(\text{CO})_{14}$ was produced, whereas higher flux irradiation yielded both $\text{H}_2\text{Re}_2(\text{CO})_8$ and $\text{HRe}(\text{CO})_5$ as the major species. Furthermore, kinetic examination of the substitution of PBu_3 for CO in $\text{Re}(\text{CO})_5$ showed CO inhibition. Together, these observations support a mechanism involving CO dissociation from $\text{Re}(\text{CO})_5$, oxidative addition of H_2 to the 15 electron $\text{Re}(\text{CO})_4$ moiety, abstraction of hydrogen by $\text{Re}(\text{CO})_5$, yielding $\text{HRe}(\text{CO})_4$. This species can then either dimerize to yield $\text{H}_2\text{Re}_2(\text{CO})_8$ or interact with two molecules of $\text{Re}(\text{CO})_5$ to give $\text{HRe}_3(\text{CO})_{14}$. Such activation of H_2 may have application to hydrogenation and hydroformylation reactions.

Similar substitution reactions have also been studied for the more reactive $\text{HMn}(\text{CO})_5$. The experimental evidence suggests a combination of mechanisms. At times, the reaction is extremely rapid, indicating a radical process. However, linear pseudo first order rate plots are observed when no radical process is involved, and a thermal reaction involving ligand dependent hydride migration appears to be operative:



Although no spectroscopic evidence for the formyl species exists, ^{13}C O exchange studies,⁴ currently being reexamined, do support such a pathway.

This research suggests a correlation exists between M-H bond strength and the reaction pathway. The stronger Re-H bond shows no tendency to undergo hydride migration. Further studies in this area may allow one to predict the mechanism of substitution by knowing the approximate M-H bond strength.

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HIGH PRESSURE THERMODYNAMIC AND SPECTROSCOPIC STUDIES ON OXYGEN STABILIZATION AND COORDINATION

Tony J. Beugelsdijk

23 June 1975

Introduction

The function of molecular oxygen as a ligand in transition metal chemistry has evoked considerable interest within the past ten years.¹ The broad spectrum of included reactions is evidenced by the efforts of chemists from quite different interests. Biochemical interest focuses on the search for model compounds for oxygen transport, for oxidases, and for the catalytic insertion of oxygen atoms derived from molecular oxygen into biological substrates.^{2,3,4} Industrial chemists search for homogeneous analogs to the current heterogeneous oxidation catalyst systems.⁵ The scope of all such investigations, however, has resulted in only a very incomplete definition of the nature of the chemical bond in terms of the thermodynamics of oxygen coordination, stabilization, and activation.

Statement of the Problem

A basic shortcoming in determining the thermodynamic parameters associated with oxygen uptake has been the choice of the experimental design. Spectroscopic titrations have been conducted over a limited fraction of the saturation range and experimental points fitted to a mathematical model which obscures non-ideal behavior and artificially smoothes observed uncertainties.⁶ An alternate method, based on an esr integration technique suffers from errors inherent in such a manipulation and the delicate dependence of esr lineshapes on experimental conditions.⁷ The ideal approach would see a maximum change in an observable per unit of perturbation on the system. In the absence of any new exotic methods, the remaining recourse is to force coverage of the saturation range under elevated pressures of oxygen. Accordingly, a high pressure optical absorption cell was constructed.

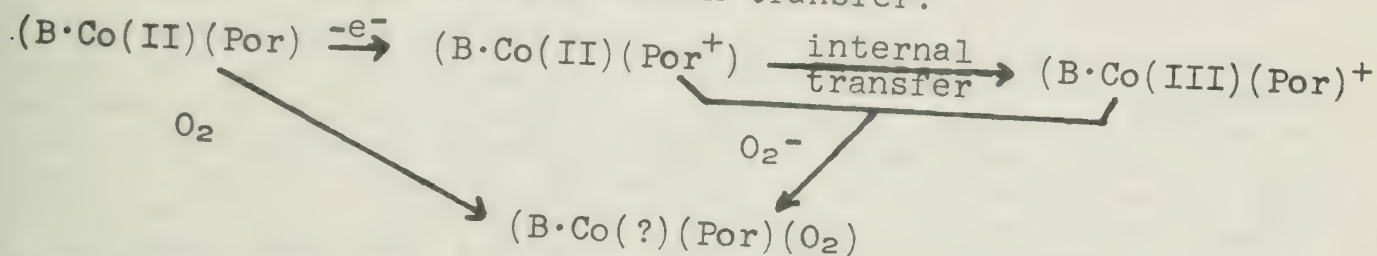
Results and Discussion

Toluene solutions of B·CoPIXDME show changes in the visible region accompanying increasing pressures of oxygen above solution characteristic of the formation of the dioxygen adduct (B=base, CoPIXDME=cobalt(II) protoporphyrin dimethyl ester). The enthalpies of adduct formation show a remarkable constancy in light of the variation of base donor atoms studied.

The failure to find a correlation between this enthalpy and the base E and/or C property⁸ may provide partial justification for the assumption of the presence of π stabilization in the interaction. Attempts to conclusively defend such a mechanism failed due to the limited choice of bases with drastically

different E numbers. This property should be expected to exert influence on the relative energies of the d orbitals of the base-metalloporphyrin adduct with the result of varying degrees of overlap with the orbitals of oxygen. This changing overlap should manifest itself in the magnitude of the enthalpy of oxygen uptake.

Electrochemical oxidation of the five-coordinate species gave two well-defined oxidation waves. The positions and difference in the potentials of the two waves show surprising constancy when the axial base was varied. This can be explained by an oxidation of the porphyrin nucleus followed by a rapid internal electron transfer:



In all cases the five-coordinate species was established in solution prior to oxidation.

Further elucidation of the prime factors underlying oxygen stabilization must await larger perturbations at the axial site. It is felt, however, that a very delicate balance exists between electronic and steric requirements that such perturbations may result in irreversible behavior toward oxygen.

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SYNTHESIS, STRUCTURAL, MAGNETIC AND CHEMICAL PROPERTIES OF LOW VALENT ORGANOMETALLIC TITANIUM COMPOUNDS

Dennis Sekutowski

FINAL SEMINAR

June 30, 1975

Low valent (less than IV) titanium organometallic compounds have been studied extensively by industry because of the economical importance of Ziegler-Natta catalysts. Recently, other workers have become interested in biscyclopentadienyl titanium systems in relationship to nitrogen fixation and carbonyl insertion reactions. Despite all of this interest, there have been only a few low valent titanium systems that have been fully characterized.

The reduction of Ti(IV) halides by various metals can lead to both Ti(III) and Ti(II) species. In the case of cyclopentadienyl derivatives, the Ti(III) species are frequently complexed to the metal halide formed from the reducing metal, to give linear mixed metal complexes of the form $(Cp_2TiX)_2MX_2$, where $X = Cl, Br$ and $M = Zn, Be$ and Mn .¹ In addition to the oxidation potential of the central metal atom, the reduction reactions are very dependent upon solvent and the nature of substitution upon the cyclopentadienyl group. These complexes are extremely oxygen sensitive and the complex $(Cp_2TiCl)_2ZnCl_2$ can be used as an oxygen monitor for an inert atmosphere dry box.²

Only a few magnetic studies have been performed upon trimetallic systems and the magnetic susceptibility studies of the $(Cp_2TiX)_2MX_2$ complexes revealed that these were the first examples of 1,3 magnetic exchange via a diamagnetic metal atom in a linear trimetallic complex.^{3,4} The effects of variation in the cyclopentadienyl ring substitution, the bridging anion X, and the central metal M upon the cooperative interactions between the titanium atoms were investigated. The magnetic behavior observed for these species is anomalous when compared to that reported for the dinuclear $(Cp_2TiX)_2$ complexes.^{5,6} A study of the magnetic and structural properties of $(Cp_2TiCl)_2$ and $(MeCp_2TiCl)_2$ were made in order to resolve the differences in the dinuclear and trinuclear systems.⁷

Another type of metal reduction product was observed in the reaction of $(Cp_2TiCl)_2$ with sodium phenylethynyl.⁸ Biscyclopentadienyltitanium phenylethynyl was previously assumed to be a dimer with the phenylethynyl groups bridging the metal atoms in either a $\sigma-\pi$ fashion or with an electron deficient three center carbon bond.⁹ The lack of a carbon-carbon triple bond stretch in the infrared spectrum and the diamagnetism of the compound do not agree with either of the above bonding descriptions. The structural work of $[MeCp_2TiC_2C_6H_5]_2$ indicates that the two phenylethynyl anions have oxidatively coupled and are complexed to two $MeCp_2Ti$ groups. The resulting complex is closely related to the uncoupled dimeric species and, on the basis of infrared studies, it is suggested that the latter is an intermediate in the coupling reaction.

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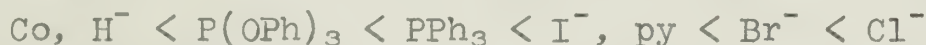
KINETICS AND MECHANISMS OF ^{13}CO EXCHANGE WITH $\text{Cr}(\text{CO})_4(\text{CHELATE})$ COMPLEXES AND RELATED COMPOUNDS

Martin A. Cohen

Final Seminar

October 7, 1975

Investigation of ^{13}CO exchange with complexes of the type $\text{Cr}(\text{CO})_4(\text{chelate})$ was undertaken to ascertain the rate ordering of ligands inducing cis labilization, and the stereochemistry of CO dissociation. Cis labilization is a phenomenon, previously noted by Brown and co-workers,^{1,2} in which a ligand coordinated to an octahedral metal center causes a rate enhancement of dissociation of the carbonyls cis to that ligand. On the basis of ^{13}CO exchange studies and substitution studies, the proposed order of cis labilization is:



This research has involved study of the ^{13}CO exchange of $\text{Cr}(\text{CO})_4(\text{chelate})$ complexes, in which chelate = phen, bipy, diphos, dpp, ape, nbd, and cod. Three types of reactions were observed under the reaction conditions employed: a) decomposition; b) chelate loss with ^{13}CO incorporation into the metal fragment; and c) ^{13}CO incorporation into the parent compound. It is proposed that, for the nbd and cod complexes, chelate loss occurs via the chelate ring-opening mechanism,³ i.e., a stepwise dissociation of the chelate ends. On the basis of the stereochemical distribution of ^{13}CO in $\text{Cr}(\text{CO})_4(^{13}\text{CO})_2$, it appears that the five-coordinate intermediate having the mono-ligated chelate is fluxional. Incorporation of ^{13}CO into the parent complexes, containing phen, bipy, diphos, and dpp, occurs via CO dissociation cis to the chelate. The intermediate $\text{Cr}(\text{CO})_3(\text{L-L})$, generated by CO loss is partially fluxional, as evidenced by a comparison of the simulations of the product distribution for either a completely rigid or completely fluxional intermediate.

An attempt to define further the labilizing effects of PPh_3 led to the exchange study of fac- $\text{Cr}(\text{CO})_3(\text{phen})(\text{PPh}_3)$ and trans- $\text{Cr}(\text{CO})_4(\text{PPh}_3)_2$. In both cases, PPh_3 was dissociated. The products of the reaction (as determined by ^{13}C NMR) were fac- $\text{Cr}(\text{CO})_3(^{13}\text{CO})(\text{phen})$ and a mixture of cis- and trans- $\text{Cr}(\text{CO})_4(^{13}\text{CO})\text{PPh}_3$, respectively. The explanation of the mixture of the cis and trans isomers is based upon the generation of a higher energy intermediate which is not readily accessible during the exchange study of $\text{Cr}(\text{CO})_5\text{PPh}_3$. Furthermore, the lifetime of the intermediate is of the same order as the rate of rearrangement to the more favored intermediate.

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LAMELLAR COMPOUNDS OF GRAPHITE

Craig S. Chamberlain

October 29, 1975

Introduction

Lamellar compounds of graphite (LCG) are composed of single layers of atoms or small molecules inserted between the parallel planar carbon layers of graphite. Inserted materials include alkali metals, transition metal halides and chalcogenides, non-metal halides and chalcogenides, halides, and acids.¹ Additionally, Klotz and Schneider² and Vol'pin and coworkers³ have reported LCG with most of the first row transition metals in the zero-valent state.

LCG have a variety of uses. They have been found to be synthetic metals, models for two dimensional magnetism, superconductors, electrodes, redox agents, and catalysts. Included in the reactions that LCG catalyze are the Fischer-Tropsch synthesis of hydrocarbons and the synthesis of ammonia.⁴ To better understand these compounds and how they function, it is important to know their structure and bonding. In this seminar, the structure and bonding in LCG of FeCl_3 , FeCl_2 , $\text{Fe}(\text{O})$, and $\text{Mo}(\text{O})$ will be examined as representative cases, these compounds being the most well characterized in their respective classes. The primary physical methods used are X-ray diffraction, magnetism, Mössbauer spectroscopy, and electrical measurements.

 FeCl_3 and FeCl_2 LCG

FeCl_3 LCG are formed by heating graphite and allowing FeCl_3 vapor to intercalate.⁵ X-ray and electron diffraction studies indicate the FeCl_3 exists in the LCG as a distorted octahedron with some Cl-C interaction.⁶ Mössbauer measurements tend to indicate that the FeCl_3 receives less than a complete electron from graphite upon LCG formation.⁷ Thus, there is apparently no major perturbation of the FeCl_3 structure upon intercalation; the FeCl_3 is weakly held in place between carbon layers.

FeCl_2 LCG are formed by reduction of the FeCl_3 LCG by heating in a stream of N_2 , Ar, or H_2 , or in a vacuum.⁸ Apparently, there is little or no bonding interaction between FeCl_2 and graphite as indicated by Mössbauer spectroscopy and the interlayer spacing determined from X-ray diffraction measurements.

 $\text{Fe}(\text{O})$ and $\text{Mo}(\text{O})$ LCG

$\text{Fe}(\text{O})$ LCG may be formed by reduction of FeCl_3 LCG or FeCl_2 LCG with a variety of reducing agents such as Na-NH_3 , LiAlH_4 , or lithium biphenyl.⁹ Mössbauer measurements indicate that the material formed is zero-valent iron which may be donating some electron density from 4s orbitals to graphite. Magnetic data indicate that the iron may either be complexed or exist as a metallic monolayer. The spacing observed by X-ray diffraction is in agreement with that expected for

van der Waals interaction between iron and carbon layers, indicating little bonding interaction. Thus, the question as to whether the iron is complexed or exists as a simple monolayer sandwiched between carbon layers is not entirely resolved.³

The bonding in the Mo(O) case is less ambiguous. This material is formed from MoCl₅ LCG in the same manner as the Fe(O) LCG.⁹ The compound is diamagnetic, in agreement with the magnetic behavior expected for a Mo(O) bis-arene complex, but not for a molybdenum monolayer. The observed interlayer spacing is much smaller than expected for van der Waal separation of the layers or for olefinic or allylic complexes with graphite. The distance is in agreement with that expected for a bis-arene complex of Mo(O). Thus, the Mo(O) LCG appears to be an example where graphite acts as a macroscopic bis-arene or bis-hexahapto pi-donor ligand.³

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MULTIPLE METAL-METAL BONDING IN TRANSITION METAL DIMERS

Jack A. Kramer

October 30, 1975

Introduction

During the last decade, there has been a dramatic increase in the number of multiply-bonded transition metal compounds characterized. Although the first reported synthesis¹ of a quadruply-bonded compound, $\text{Cr}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$, was in 1844, over 120 years passed before it was recognized² that such compounds are quadruply-bonded metal dimers.

In 1963, Russian workers reported³ an unusual single-crystal X-ray structure for a compound with the empirical formula $(\text{pyH})\text{HReCl}_4$. The rhenium ions are separated by only 2.24 Å, and are positioned in the center of a nearly cubic array of chloride ions. This short Re-Re distance seemed quite unlikely in light of distances of 2.48 Å in Re_3Cl_9 ⁴ and 2.75 Å in rhenium metal.

F. A. Cotton et al.⁵ determined the crystal structure of " $\text{KReCl}_4 \cdot \text{H}_2\text{O}$ ", which confirmed the Russians' observations. He then proposed² a quadruple bond to account for the extremely short Re-Re distance and the eclipsed conformation of the chlorides.

Occurrence

In order to form metal-metal bonds, several conditions must be met;⁶ the metal must a) be in a low oxidation state: high oxidation states lead to contracted d orbitals which don't allow the necessary overlap, and b) lie on the left of the periodic table. This prevents too large a contraction in the d orbitals and population of anti-bonding orbitals.

Using these guidelines, a considerable number of compounds⁷ containing Re, Mo, Cr, Tc, Rh, Ru, Fe, and W have been found which have multiple metal-metal bonds. Mixed metal compounds containing Mo and W⁸ and Cr and Mo⁹ have been reported.

Also, multiple metal-metal bonds are found in compounds with Br^- , Cl^- , SCN^- , SeCN^- , $-\text{CH}_3$, $\text{C}_4\text{H}_8^{2-}$, π -allyl, $-\text{O}_2\text{CR}$, $\text{P}(\text{C}_2\text{H}_5)_3$, $\text{PhC}(\text{NPh}_2)_2$, and others as ligands. This shows the wide range of such compounds.

Bonding

It was proposed² that the quadruple bond has one σ , two π , and a δ component. The σ bond is formed by overlap of d_{z^2} - p_z hybrids of each metal atom. The two equivalent π bonds are formed from overlap of the degenerate d_{xz} and d_{yz} orbitals, and the δ bond from overlap of the d_{xy} orbitals. Only the δ bond is angle dependent, the others being cylindrically symmetrical about the metal-metal axis. The chlorides must be eclipsed for maximum overlap of the d_{xy} orbitals. The s, p_x , p_y , and $d_{x^2-y^2}$ orbitals are used to bond to the "equatorial" ligands.

The essentials of this bonding scheme have been verified by extended Hückel MO calculations¹⁰ and SCF-X α SW calculations¹¹ on (Re₂Cl₈)²⁻, and SCF-X α SW calculations¹² on (Mo₂Cl₈)⁴⁻, although some details are still being debated.

Many physical techniques have been used to probe the multiple metal-metal bonding, among them X-ray diffraction,⁷ magnetic susceptibility,¹³ and photoelectron,¹⁴⁻¹⁵ visible-UV,¹⁶ epr,¹⁶ nmr,¹⁷ IR,¹⁸⁻²¹ and Raman¹⁸⁻²² spectroscopies.

Properties

Compounds with multiple metal-metal bonds are generally air sensitive in solution, but relatively stable as solids. Solutions of Rh₂⁴⁺(aq) are particularly stable, however, and may be handled in air.²³

{Re₂Cl₄[P(C₂H₅)₃]₄}²⁺ may be reduced in solution to the +1 and 0 species,²⁴ but oxidation or reduction of most other compounds with multiple metal-metal bonds leads to unstable products.

Protonation of Rh(II), Ru(2.5), or Mo(II) carboxylates and addition of triphenylphosphine forms complexes which catalyze hydroformylation and carbonylation reactions, and the hydrogenation of olefins and acetylenes, either homogeneously or heterogeneously on cation-exchange materials.²³

Summary

Formation of multiple metal-metal bonds is an important aspect of the low-valent chemistry of many transition metals. They offer many opportunities to study metal-metal interactions as a function of the metals and ligands involved, as well as being useful catalysts for a number of reactions. There is much yet to be discovered about this unique class of compounds.

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MAGNETIC CIRCULAR DICHROISM

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November 5, 1975

Introduction

Magnetic optical activity, discovered by Michael Faraday in 1845, has proven to be a powerful technique in studying both the ground and excited electronic states of transition metal complexes. In this seminar, we are concerned with those aspects of magnetic optical activity known as magnetic circular dichroism (MCD). Although the theoretical basis of MCD was available by 1965¹⁻³ and a few experiments had been done in the optical rotatory dispersion mode, major experimental advances did not come about until the introduction of commercial CD instrumentation and superconducting magnets in the mid-sixties. Thus, most experimental MCD is quite recent. A review of the theory and applications of MCD has recently been published.⁴

Theory

In general, the form of an MCD line is given by:

$$\theta_m = - 21.346 (f^0 A + f' B + \frac{f' C}{kT})$$

where θ_m is the molar ellipticity, A, B and C are the Faraday terms and f^0, f' are lineshape functions. For certain simplifying assumptions, the A,B,C terms are given by:

$$A = \frac{3}{2d_a} \sum_{a,j} [\langle j | \mu_z | j \rangle - \langle a | \mu_z | a \rangle] [| \langle a | m_+ | j \rangle |^2 - | \langle a | m_- | j \rangle |^2]$$

$$B = \frac{3}{d_a} \sum_{a,j} \left\{ \sum_{k \neq a} \frac{\langle k | \mu_z | a \rangle}{E_k - E_a} [\langle a | m_+ | j \rangle \langle j | m_- | k \rangle - \langle a | m_- | j \rangle \langle j | m_+ | k \rangle] \right. \\ \left. + \sum_{k \neq j} \frac{\langle j | \mu_z | k \rangle}{E_k - E_j} [\langle a | m_+ | j \rangle \langle k | m_- | a \rangle - \langle a | m_- | j \rangle \langle k | m_+ | a \rangle] \right\}$$

$$C = \frac{3}{2d_a} \sum_{a,j} \langle a | \mu_z | a \rangle [| \langle a | m_+ | j \rangle |^2 - | \langle a | m_- | j \rangle |^2]$$

Another term of frequent interest is the dipole strength:

$$D = \frac{3}{2d_a} \sum_{a,j} [| \langle a | m_+ | j \rangle |^2 + | \langle a | m_- | j \rangle |^2]$$

An A term is possible, i.e., non-zero, whenever the ground or excited states of the transition are electronically degenerate. The magnetic field splits the degeneracy causing the right circularly polarized and left circularly polarized components of the transition

to occur at different energies. The C term arises when the ground state is degenerate. The magnetic field splits the degeneracy causing a repopulation of levels according to Boltzmann statistics. The B term arises from field-induced mixing of the ground and excited states with other electronic states. This is the same effect that causes temperature independent paramagnetism. It is experimentally possible to separate an MCD spectrum into its component A,B,C terms if one measures the spectrum over a range of temperatures.

Applications

The simplest use of MCD lies in it being an alternate technique for detecting optical transitions. Relative intensities of bands in MCD are different from normal absorption spectroscopy making it possible to detect some transitions better with MCD than with absorption. In particular, it is possible to detect spin-forbidden transitions with MCD which are often weak or even undetectable otherwise.⁵ The resolution of bands in MCD is potentially better since both positive and negative bands occur. MCD has considerable value in distinguishing electronic from vibrational transitions in the IR since the latter show much weaker MCD. This is particularly applicable to transition metal complexes.

MCD has found considerable use in assigning electronic transitions of transition metal complexes. The presence of an A or C term is immediate evidence that a degenerate state is involved. For example, Stillman and Thomson have shown that the presence of a negative A term in the MCD spectrum of Fe(II)phthalocyanine in dichlorobenzene solution leads to the assignment of a $^3A_{2g}$ ground state.⁶

Most often the ground state is well-known, but the nature of the excited state is less certain. Here, comparison of experimental and theoretical values of A,B and/or C allows the assignment of the correct excited state to the transition. For example, Schatz and co-workers⁷ have applied this technique to the charge-transfer bands of $\text{Fe}(\text{CN})_6^{-3}$ and MnO_4^- . From the sign of the observed C terms for $\text{Fe}(\text{CN})_6^{-3}$, they were able to assign the symmetries of the excited states. For MnO_4^- , they were able to lend weight to one previous assignment and show that another assignment was incorrect.

Once the assignment of a transition has been achieved, the use of experimental A values allows one to calculate excited state magnetic moments. Such data is quite difficult to obtain by other means. Since the excited state magnetic moment is quite sensitive to Jahn-Teller effects, spin-orbit coupling and covalency effects, MCD is a sensitive probe of these effects. Stillman and Thomson have used MCD to measure the excited state magnetic moments of a series of metal phthalocyanines where the central metal was varied.⁸ They ascribed the variations in the magnetic moment to various amounts of metal-ligand covalency. Similarly, McCaffery, Stephens and Schatz found small values of the excited state magnetic moment for several Co(III) and Cr(III) complexes and postulated a quenching of the orbital angular momentum in the excited states by Jahn-Teller interactions.⁵

Additional applications include the elucidation of intensity mechanisms in the case of forbidden d-d transitions,^{5,9} and some work has been done in probing interactions between two metal centers.^{10,11} MCD has occasionally been used for identification of unknown species.¹² As in absorption spectroscopy, the greatest amount of information is obtained from oriented samples at low temperatures where individual vibrational components are resolved. Such studies are becoming more prevalent.¹³

It is obvious that MCD is a powerful tool in studying both the ground and excited states of transition metal complexes of high symmetry. MCD gives certain information more readily than other techniques and other data which are obtainable in no other way. MCD is a relatively new field experiencing rapid growth and promises to make significant contributions in the future.

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INTERNAL METALATION OF PHOSPHORUS LIGANDS

R. Joe Lawson

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Ligand and Metal Requirements

Currently there is much interest in activating carbon hydrogen bonds.¹ Intramolecular activation of carbon hydrogen bonds occurs in transition metal complexes containing ligands coordinated through a Group V element. Only a few examples are known for arsines,^{2,3} but much work has been done on systems containing amines, azobenzenes, phosphines and phosphites.⁴⁻¹⁵ With aromatic amines and Schiff bases, the internal, or intramolecular, metalation is believed to take place by electrophilic substitution at the ortho ring position with the metal acting as the electrophile. In the case of phosphines and phosphites, however, many examples are thought to occur via oxidative addition in which the metal is nucleophilic.⁴

Internally metalated species have been isolated for all Group VIII metals except nickel, and species involving manganese have been reported.⁴⁻⁸ The activated hydrogen is usually aromatic, but internal metalations of primary, secondary and tertiary carbons have been observed.⁹ Metalation at an aromatic carbon is, however, much faster than at an aliphatic carbon.¹

With phosphorus ligands, it is common to see either four or five membered rings formed, but in cases that both are possible, five membered rings are strongly favored. Thus, metalation involving complexes of $P(CH_3)_2(1\text{-naphthyl})$ occurs exclusively at the 8 position of the naphthyl moiety to give five membered rings.¹⁰ Bulky groups, such as tert-butyl, on phosphines have been shown to induce metalation even though the bulky group itself is not metalated. For example, trans- $PtI_2(PBu_2Ph)_2$ metalates at the ortho position of the phenyl ring, but cis- $PtI_2[P(CH_3)_2Ph]_2$ does not metalate. It has been proposed that this is due to an entropy effect. Since rotation is already hindered in the bulky phosphines, there is little entropy loss upon ring formation.^{11,12}

Several dimetalated species have been isolated, usually with a third row transition metal. With iridium, two trimetalated species have been observed.^{5,10,13,14}

Physical Studies

Often the metalated and unmetalated species are in equilibrium under H_2 pressure. This can be easily observed by using D_2 and monitoring the HD and H_2 formed or by checking the complex for deuterium incorporation. Deuterium incorporation has been used as evidence that metalation occurs, even if the metalated species cannot be isolated. Using $RuHCl(PC_6H_5)_3$, one can catalytically ortho deuterate $P(C_6H_5)_3$. In coordinatively saturated complexes, which promote hydrogen deuterium exchange, addition of excess ligand slows or stops the exchange.¹⁵

Metalation at an aromatic carbon can be detected by ir; peaks corresponding to an ortho substituted benzene are observed.¹³ The stereochemistry is usually determined by ^{31}P nmr spectra, although

in some hydrides only the ^1H nmr spectra with ^{31}P coupling have been used.^{10,13}

Conclusions

These studies have shown that metal complexes can aid in activating carbon hydrogen bonds. It is hoped that continued investigations will lead to systems that catalyze substitution of aromatics, or even alkanes, by metalated intermediates.

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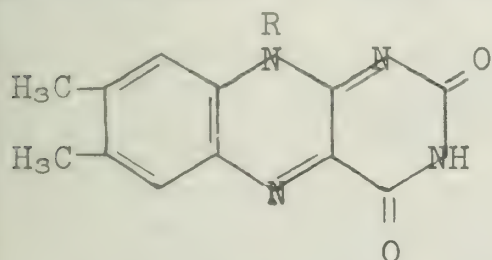
METAL FLAVOENZYMES AND MODEL SYSTEMS

Karen Lynn Hassett

November 25, 1975

Molybdenum was the first metal discovered to be a component of a purified flavoenzyme, xanthine oxidase, in 1953.¹ In the intervening 22 years, there has been a considerable amount of interest in the exact role which metals play in enzymatic catalytic activity.^{2,3,4}

Certain enzymes contain at least two types of prosthetic groups, or non-protein parts of the enzyme which are tightly bound to the protein. These are the metalloflavoenzymes, which contain both a metal (Fe, Mo, and/or Zn) and a flavin. The two flavins commonly found are FAD (flavin adenine dinucleotide) and FMN (flavin mononucleotide). The structures of these two groups are as follows:



FAD: $R = \text{CH}_2(\text{CHOH})_3\text{CH}_2\text{O}(\text{PO}_3\text{H})_2\text{-adenosine}$

FMN: $R = \text{CH}_2(\text{CHOH})_3\text{CH}_2\text{OPO}_3\text{H}_2$

Flavoenzymes have not proved easy to study. Their molecular weights are on the order of 300,000 g/mole, and they have, by definition, at least two non-protein groups in addition to a long protein chain. The most useful probe into the inner workings of these enzymes has thus far been electron paramagnetic resonance. Using this technique, many different species containing unpaired electrons have been found. Molybdenum was one of the first to be identified definitely⁵ because of its characteristic six-line hyperfine splitting (25% of natural abundance molybdenum has $I = 5/2$). As techniques of epr have improved, more has been discovered about the epr-active species in the enzymes. Not only is it known that Fe(III) is involved in the catalytic activity, but there are two or four distinguishable iron sites in some enzymes.^{6,7} A note of caution is appropriate here, because although a good deal has been learned about the enzymes through the use of epr spectroscopy, it is still true that no more than 20% of the total Mo, for example, has been accounted for in measurements on fully reduced enzymes.⁸ If all of the molybdenum were participating simultaneously in the oxidation of the substrate, 100% Mo would show epr signals (assuming that it is being reduced to the Mo(V) state, as is widely accepted for some Mo containing enzymes).⁴

Other detailed studies have seemingly elucidated the path that the electrons take during some oxidations,^{9,10} however, recent investigations have questioned the validity of some of these results.¹¹

Since the detailed structure of these enzymes has thus far been too complicated for present techniques, many models which represent the prosthetic groups in the proteins have been made. The specific models under consideration here are the ones which mimic the possible direct interaction between the flavin and metal. Two types of model systems have been looked at; those with a complete flavin structure,

such as riboflavin where the R in FAD or FMN is replaced by $\text{CH}_2(\text{CHOH})_3\text{CH}_2\text{OH}$, and also a series of 8-hydroxyquinones. The X-ray structures,^{12,13} electrical properties,^{14,15} and nuclear magnetic resonance spectra^{16,17} of these compounds have been studied extensively.

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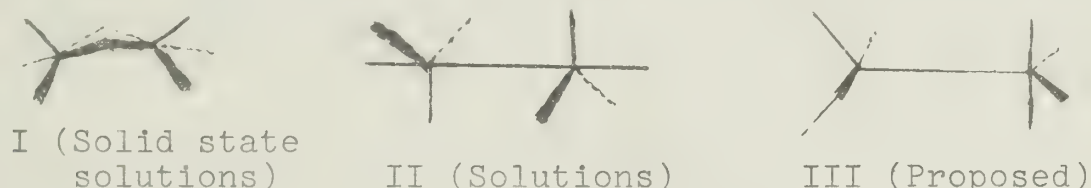
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THE USE OF MATRIX ISOLATION SPECTROSCOPY IN THE CHARACTERIZATION OF DICOBALT OCTACARBONYL

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Currently two isomers of dicobalt octacarbonyl are well enough characterized to have been accepted as real. Crystallographic studies have shown one of the isomers (I) to have two carbonyl ligands bridging the metals as shown below.¹ A second isomer (II) is generally acknowledged to be of D_{3d} symmetry with no bridging carbon monoxide.² Recently, it has^{3d} been pointed out that the two isomers could not produce all the bands which have been observed in solution infrared spectra. A third isomer has been postulated. Raman evidence also supports the existence of a third isomer.³ Observation of the ^{13}C nmr spectra have not been useful in studying the isomers of $Co_2(CO)_8$ because of rapid interconversion between the isomers.⁴

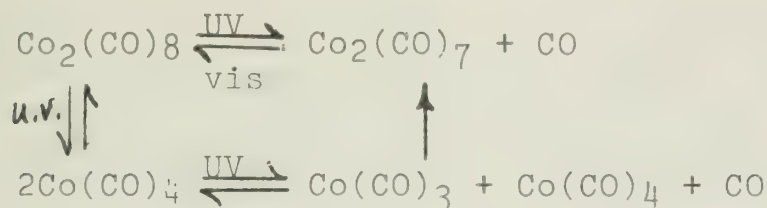


The three isomers of $Co_2(CO)_8$ are easily differentiated using matrix isolation spectroscopy. Matrices of $Co_2(CO)_8$ are formed by co-depositing gaseous $Co_2(CO)_8$ and a matrix gas on a sodium chloride support which is cooled by either liquid helium or nitrogen. The matrix gases used for this study were Ar, Ne, N_2 , O_2 , CO, CH_4 , isobutane and hexane. The bands of the spectrum were assigned to their respective isomers by observing the intensity variation of the bands after the matrices were photolyzed by ultraviolet and visible radiation. There are three clearly differentiated sets of infrared bands, two of which correlate with the isomers discussed in the introductory paragraph. The third set of bands is assignable to a third isomer. We have tentatively assigned a structure of D_{2d} symmetry to the third isomer (III, see above).

The slow conversion of II to I has been observed in hexane matrices at 83°K. The rate constant for the transformation is $2.4 \pm .2 \times 10^{-4} s^{-1}$. The free energy of activation for the process is $6.3 \pm .4$ kcal/mole. Isomer III is not observed in measurable concentrations in hexane even when the matrix is cooled with liquid helium. Its conversion to one of the other two isomers must be extremely rapid even at very low temperatures. An estimate of $\Delta G^\ddagger \pm 2.5$ kcal/mole for such conversions seems consistent with the data.

Photolysis of $Co_2(CO)_8$ yields new bands which are assigned to $Co_2(CO)_7$. The detailed structure of $Co_2(CO)_7$ cannot be deduced from the spectrum. However, the absence of bands due to bridging carbonyls suggests the structure may be described by $(CO)_4Co-Co(CO)_3$. Photolysis of $Co_2(CO)_8$ in CO matrices differs from the photolysis in other matrices. $Co(CO)_4$ is observed when CO matrices are photolyzed as well as $Co_2(CO)_7$.

A mechanism which is consistent with the data appears below.



Pyrolysis of $\text{Co}_2(\text{CO})_8$ in the gas state yields a product tentatively identified as $\text{Co}_2(\text{CO})_6$. The spectrum is consistent with a triple metal-metal bond. Interestingly, very little $\text{Co}_2(\text{CO})_7$ is observed under the same conditions.

The results of the matrix experiments will be discussed in relation to the observed behavior of $\text{Co}_2(\text{CO})_8$ as described in several recent kinetic studies.

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POSITRON ANNIHILATION SPECTROSCOPY

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January 20, 1976

Implantation of positrons into solids, liquids, or gases results in the production of gamma radiation from the annihilation of the positrons with the electrons in the sample. The rate of annihilation and the energy and angular distribution of the gamma rays produced can provide a wealth of information concerning both the chemical and physical environment of the electrons which are annihilated. To date, positron annihilation spectroscopy has mainly been confined to solid state applications, but the chemistry which has been studied using this technique indicates that it has great potential in chemical applications as well and could develop into as important a tool to the Inorganic chemist as Mössbauer, ESCA, and other experimental techniques.

Positrons are emitted from man-made nuclei deficient in neutrons such as $^{22}_{11}\text{Na}$ with kinetic energies of around 1 MeV. They are rapidly thermalized in most materials and can then either annihilate with the electrons in the medium as free positrons or as positronium, which is an electron-positron bound pair. Ortho (triplet) positronium annihilates in around 10^{-7} sec. to produce three gamma rays. Para (singlet) positronium and the majority of the free positrons annihilate via a two gamma process in around 10^{-10} sec. These annihilation times depend on the electron density of the medium in all cases. The lifetime of ortho positronium can also be shortened significantly by conversion to para positronium due to a collision with a paramagnetic center, or through a variety of chemical reactions such as oxidations, reductions, substitutions, and additions. Thus, much of the chemical information obtainable from a given sample is derived from a study of the annihilation of ortho positronium.

Positron annihilation spectroscopy has to date involved four basic experimental techniques, all of which involve detection of the gamma radiation produced in the annihilation process. Rates of annihilation are measured using the lifetime experiment, which employs a positron source such as $^{22}_{11}\text{Na}$ which emits a gamma ray at the same time it emits a positron. The time lag between the moment the "time marker" gamma ray is detected and the moment gamma rays produced by annihilation of the positron are detected gives the lifetime of the positron in the sample. Detection of changes in the relative amounts of ortho positronium formed is possible using a triple coincidence apparatus which detects all three gamma rays produced in the annihilation simultaneously. The momentum distribution of the electrons which are annihilated can be obtained either by doing an angular correlation experiment to measure the deviation from 180° in the angle between the gamma rays produced in the two gamma annihilation, or by analyzing the Doppler line shape of the 0.51 MeV centered gamma annihilation band. Until recently, all of the above techniques were used independently of one another, but use of the techniques together should also prove to be of great value.

Positron annihilation has a wide range of capabilities, most of which have not as yet been exploited to the extent that they should be. With this method, it is possible to detect the presence of free radicals and paramagnetic species with great sensitivity. Spin delocalization onto

the ligands of inorganic complexes can be detected. Positronium reactions can be used to determine the kinetic parameters for a variety of chemical reactions in solution. The method can be used to measure and identify defects and impurities in solids. Surface chemistry studies should also be possible. Phase transitions can be studied in detail by using positrons. Momentum distributions of the electrons in solids especially can be used in a variety of solid state and chemical applications including determination of band structure and spin polarizations in metals and semiconducting materials, Compton scattering applications, and others. The above list of applications is by no means complete and continues to grow as more investigations into the interactions between positrons and matter are carried out. Production of commercial instrumentation, improvements in instrument resolution, coupling of the various spectroscopic techniques, and development of new positron techniques employing such additions as magnetic fields are all needed if the method is to have the impact on the world of chemistry that it deserves. These coupled with a growing interest among chemists in the method should make positron annihilation spectroscopy one of the primary tools of the physical inorganic chemist within the next decade.

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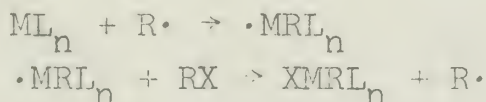
FREE RADICAL REACTIONS OF TRANSITION METAL ORGANOMETALLIC COMPOUNDS

Jerry Keister

February 10, 1976

Most mechanisms of transition metal organometallic reactions are based on simultaneous two-electron changes in oxidation state of diamagnetic (usually 16- or 18-electron) systems. Exceptions have been redox reactions of organic radicals with metals which act as one-electron transfer agents (Fe(II), Cr(II), Cu(I), Co(II)). The first compound for which a rich chemistry involving radicals was established was $\text{Co}(\text{CN})_5^{-3}$, a 17-electron species which undergoes a variety of reactions, including oxidative addition of organic halides and hydrogenation of olefins, by radical processes.¹ Only recently have free radical intermediates been shown for other systems in reactions involving oxidative addition^{2,3} and reductive elimination,¹⁵ hydrogenation,¹⁴ insertion,¹⁶ metal-metal bond formation and cleavage,⁸ and substitution.¹⁰⁻¹³ Studies of these radical mechanisms have been greatly aided by knowledge about reactivity of organic radicals and by techniques developed in conjunction with the study of organic radicals.

One of the most extensively studied reactions in organometallic chemistry is oxidative addition of alkyl and aryl halides to metal centers. This process has been shown to proceed by $\text{S}_{\text{N}}2$ displacement for many systems.² However, Osborn and coworkers³ have shown that in certain cases this reaction can occur by a radical chain mechanism which is proposed to be:



This is indicated by the effects of free radical inhibitors and initiators on the rate of reaction. The reaction results in loss of stereochemistry at the carbon center, in contrast to an $\text{S}_{\text{N}}2$ type process, which gives inversion of configuration. In favorable cases, CIDNP⁴ enhanced absorption and emission, characteristic of free radical diffusive encounters, is noted in the nmr of the organic products. The presence of organic radical intermediates is also shown by their characteristic rearrangements and by hydrogen atom abstractions in good donor solvents. In other systems, free radical spin traps, such as *t*-butylnitroxide, have been used to trap the radical intermediates as relatively long-lived nitroxide radicals identifiable by esr spectroscopy.⁵ However, the reaction mechanism is extremely dependent on the metal, its ligands, and the substrate. For example, $\text{Ir}(\text{CO})\text{Cl}(\text{PMe}_3)_2$ reacts with BrCH_2CHPh by a free radical process but apparently by $\text{S}_{\text{N}}2$ displacement with CH_3I .

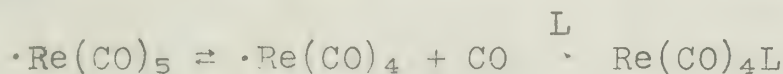
Another way in which metal-centered radicals can be generated is by homolytic cleavage of metal-metal bonds. In view of the radical chemistry of $\text{Co}(\text{CN})_5^{-3}$, it is perhaps not unexpected that its 17-electron metal carbonyl analogs ($\text{Co}(\text{CO})_4$, $\text{Mn}(\text{CO})_5$, $\text{Re}(\text{CO})_5$, $\text{Fe}(\text{CO})_3(\pi\text{-C}_3\text{H}_5)$, $\text{Mo}(\text{CO})_3\text{Cp}$) would behave similarly. The existence of such species is well established. $\text{Co}(\text{CO})_4$ has been identified by its esr spectrum in a freshly sublimed sample of $\text{Co}_2(\text{CO})_8$ ⁶ and $\text{Re}(\text{CO})_3(\text{PMePh}_2)_2$ ⁷ and other disubstituted derivatives have been isolated and characterized. Wrighton and others⁸ have studied the photochemistry of metal dimers, including

$M_2(CO)_{10}$ ($M = Mn, Re$) and $[M(CO)_3Cp]_2$ ($M = Mo, W$) and substituted derivatives. Irradiation at the wavelength of the electronic transition assigned to the $\sigma \rightarrow \sigma^*$ transition of the metal-metal bond results in reversible homolytic cleavage. The radical nature of the products is revealed by their reactions with alkyl halides to produce the corresponding mononuclear metal halides and the organic radical. Lappert and coworkers⁹ have succeeded in trapping and identifying the metal-centered radicals using large quantities of the spin trap nitrosodurene during photolysis of metal dimers.

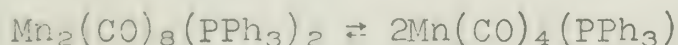
Recently, such 17-electron species have been proposed as intermediates in substitution reactions. Byers and Brown¹⁰ studied the substitution of $HRe(CO)_5$ with phosphines and proposed that $Re(CO)_5$ is an intermediate in a radical chain substitution:



This reaction is inhibited by duroquinone and can be initiated by photolysis of small amounts of $Re_2(CO)_{10}$. In another study, these authors found that photolysis of $Re_2(CO)_{10}$ in the presence of PBu_3 forms $Re_2(CO)_8L_2$ and $Re_2(CO)_9L$, in addition to $Re(CO)_3L_2$, and, at constant light flux, the rate of substitution is independent of $[PBu_3]$ and is inhibited by CO .¹¹ This was interpreted in terms of a dissociative substitution:

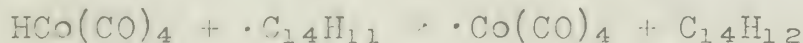


In contrast, Poë, et al.,¹² have proposed that thermal substitution of $Mn_2(CO)_8(PPh_3)_2$ by $P(OPh)_3$ to form $Mn_2(CO)_8(PPh_3)(P(OPh)_3)$ proceeds by an associative displacement:



This was based on the increase in the rate of substitution with increasing $[P(OPh)_3]$ up to a limiting value that is identical to that for its reaction with CO . A 17-electron intermediate has also been shown for the reaction $Co(CNMe)_5^+ + TCNE \rightarrow Co(CNMe)_4(TCNE)^+ + CNMe$.¹³ The intermediary of $Co(CNMe)_5^{+2}$ and $TCNE^-$ has been demonstrated but the mechanism of substitution is not known.

Metal-centered radicals have been implicated in the hydrogenation of polycyclic aromatic hydrocarbons by $HCo(CO)_4$ under "oxo" conditions.¹⁴ The mechanism proposed is:



The mechanism is similar to that proposed for the hydrogenation of 1,3-dienes by $HCo(CN)_5^{-3}$ and accounts for the nearly equal amounts of cis and trans addition products observed and for the increase in rate with substitution at the hydrocarbon.

A variety of other reactions have been shown to involve free radical intermediates but have not been investigated in depth. Cu(I) and Ag(I) alkyls in which there are no β -hydrogens present decompose by homolytic cleavage of the metal-carbon bond.¹⁵ Insertion of O₂ into the cobalt-carbon bond of B₁₂ model compounds¹⁶ and oxidation of zirconium alkyls to the alkoxides¹⁷ appear to proceed via alkyl radical intermediates. Recently, the 17-electron Fe(π -C₃H₅)(CO)₃ has been shown to be a catalyst for the isomerization of 1-hexene to trans-2-hexene without CO dissociation.¹⁸ The mechanism is not known, but commonly proposed isomerization pathways are not completely satisfactory for this reaction. It is likely that further studies will show that radical processes for organometallic reactions are more common than has been believed.

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THE METAL BINDING SITES OF TRANSFERRIN

Steve Kessel

February 24, 1976

Introduction

The existence of a unique iron bearing protein, human serum transferrin (Tf), was established in 1947.^{1,2} This iron binding protein is but one of a family of such proteins, known as the transferrins or siderophilins. As it does not contain a prosthetic group, such as heme, it must chelate the iron directly via the amino acid side chains. Serum transferrin serves several functions, the most important of which is the transport of iron to the hemoglobin synthesizing reticulocytes. It also possesses effective iron buffering capabilities and bacteriostatic activity.⁵

The protein may be conveniently isolated by employing any two of the following techniques: alcohol fractionation, ammonium sulfate precipitation, ion exchange chromatography, electrophoresis, and gel filtration.³

General Physical Properties

Early molecular weight determinations of transferrin based on ultracentrifugal measurements yielded values of 68,000 to 93,000 daltons. More recent studies, though, have suggested a molecular weight of 76,600.⁴ Based on intrinsic viscosity measurements, the B-globulin appears to resemble a prolate ellipsoid. It is capable of specifically binding two atoms of iron per molecule.^{3,5,6}

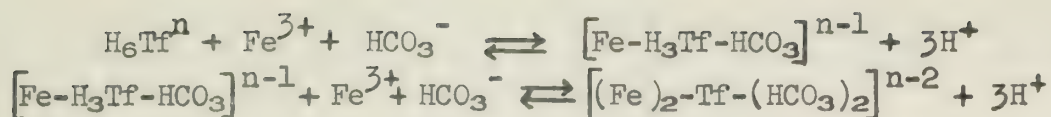
Chemical Composition and Structure

The amino acid composition has been determined by several laboratories.^{3,7} Degradation of the protein into peptide fragments has been accomplished by enzymatic digestion and CNBr cleavage, but the complete sequence has not been determined.^{8,9} The crystallographic unit cell parameters have been determined, but due to the difficulty in procuring satisfactory crystals, the detailed crystal structure has not been resolved.¹⁰

Transferrin appears to consist of a single polypeptide chain with no tendency to aggregate or dissociate in solution.⁴ It should be pointed out that serum transferrin, as well as the other siderophilins, consists of approximately 5% carbohydrate and hence is classified as a glycoprotein.¹¹

Metal Binding Sites

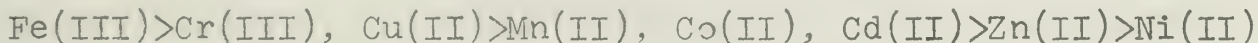
Serum transferrin reacts with iron in the presence of HCO_3^- to produce a red colored complex. The uptake of iron has been shown to be stoichiometric, with two atoms of Fe specifically binding to each molecule of protein.³ The overall reactions may be written in the following form:^{5,6}



$$\begin{aligned} K_1 &= \frac{[\text{Fe}-\text{H}_3\text{Tf}-\text{HCO}_3]^{n-1} [\text{H}^+]^3}{[\text{H}_6\text{Tf}^n] [\text{Fe}^{3+}] [\text{HCO}_3^-]} \\ K_2 &= \frac{[(\text{Fe})_2-\text{Tf}-(\text{HCO}_3)_2]^{n-2} [\text{H}^+]^3}{[\text{Fe}-\text{H}_3\text{Tf}-\text{HCO}_3]^{n-1} [\text{HCO}_3^-] [\text{Fe}^{3+}]} \end{aligned}$$

The prevalent view for some time was that Fe^{3+} ions went on and off the apoprotein two at a time. More recent experiments have indicated otherwise, that apotransferrin, monoferric transferrin, and diferric transferrin must all simultaneously exist.^{15,16} The formation constants are quite high ($\approx 10^{30}$) and appear to be almost equivalent.¹⁷

A number of multivalent metallic ions will complex with Tf. Fe(III), Zn(II), Cr(III), Co(II), Cu(II), Mn(II), and many others, including certain rare earth metals, are tightly and specifically bound by Tf.¹³ Some of the metals have been ordered in terms of stability of metal-protein complex by displacement studies.⁶



The nature of the reacting groups involved in the binding of the metals has been studied by a variety of means, including chemical modification of amino acid residues, spectrophotometric titration, visible, ultraviolet, infrared, fluorescence, ORD, CD, NMR, and ESR spectroscopy. Overall, the evidence indicates that three tyrosyl residues, two to four nitrogen ligands (presumably histidine), and one bicarbonate ion are involved in the binding of a metal ion at each site.

Tf shows two intense absorption bands in the ultraviolet and visible region. The red ferric transferrin complex exhibits absorption maxima at 280 nm ($E_{1\%}^{1\text{cm}} = 14.3$) and 468 nm ($E_{1\%}^{1\text{cm}} = 0.57$).³ The origin of these bands is still not clearly understood. The visible band may be tentatively assigned to a phenolate Fe(III), $p\pi-d\pi^*$ charge transfer transition.¹² As illustrated by optical rotary dispersion and circular dichroism studies, both absorptions are optically active.^{13,14}

Magnetic susceptibility data has shown that the bound iron is in the high spin ferric state.^{18,19,14} Little, if any, interaction transpires between the bound metal ions, as depicted by the static magnetic susceptibility. The ESR spectrum of the iron-bicarbonate-transferrin complex is characteristic of the class of Fe(III) compounds in which iron is in a site of rhombic symmetry. It consists of a three component almost isotropic line-shape centered around $g' = 4.3$ and two less intense anisotropic transitions around $g' = 9$ and $g' = 1.5$.^{20,21,15} Attempts have been made to evaluate the spectrum by theoretical calculations, using the spin-Hamiltonian

$$\mathcal{H} = g\text{BH} \cdot \hat{S} + D[\hat{S}_z^2 - 1/3S(S+1)] + E(\hat{S}_x^2 - \hat{S}_y^2).^{22,23}$$

The primary feature of the spectrum, which occurs in the region around $g' = 4.3$, arises from transitions within the middle Kramer's doublet. A zero field splitting value of 1.6 ± 0.01 °K, with $D = 0.32 \text{ cm}^{-1}$ and $\lambda = 0.315$ best explains the experimental data.²⁰

While it was believed for some time that Tf would bind iron even in the absence of bicarbonate,^{3,24} it is now reasonably certain that HCO_3^- or some other suitable anion is required for complete complexation. ESR spectroscopy has revealed that while HCO_3^- is the preferred anion,²⁵ EDTA, nitrilotriacetate, oxalate,²⁴ malonate, and thioglycolate²⁵ are all capable of inducing chelation of iron by Tf. The question as to the equivalency or nonequivalency of the two binding sites has also been cleared up by use of ESR. Replacement studies of Cr(III) bound to Tf clearly indicate a difference in the ligand field imposed by the two sites.¹⁴ Evidence that Fe(III) is also bound by nonidentical sites has been provided by ESR saturation techniques. Yet further evidence corroborating this has been presented by studying the ESR spectrum of iron-bicarbonate-transferrin as a function of perchlorate concentration.²⁶

The ESR spectrum of Cu(II) bound to Tf is indicative of a spin = 1/2 system in an axial environment.¹⁵ The substantial decrease in zero field splitting of Cu(II) compared to Fe(III) is manifested in the appearance of superhyperfine splitting in the copper spectrum, implying the presence of nitrogen ligands.²¹

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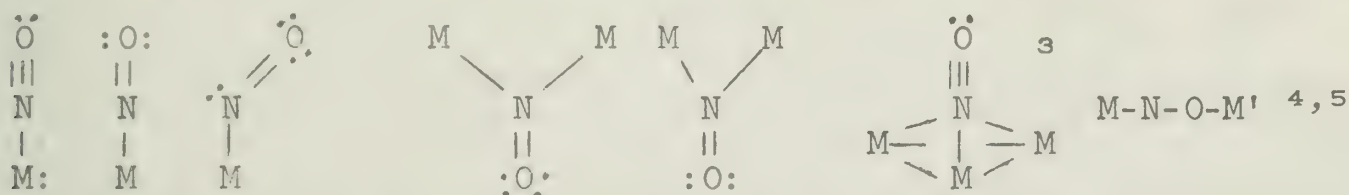
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REACTIONS OF COORDINATED NITROSYLS

Jan Peter Frick

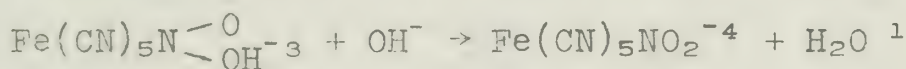
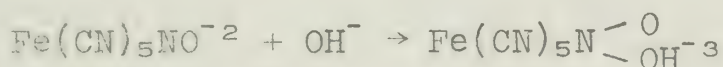
March 11, 1976

Interest in the reactions of nitric oxide coordinated to transition metals has increased in the last few years.¹ This increase is partly due to the discovery by D. J. Hodgson and J. A. Ibers that $\text{IrCl}(\text{CO})(\text{NO})(\text{P}(\text{C}_6\text{H}_5)_3)_2\text{BF}_4$ has an Ir-N-O bond angle of 124° . This discovery led to a number of crystal structures that showed that the M-N-O angles can vary from 120° to 180° . The different types of nitrosyl bonding are shown below:



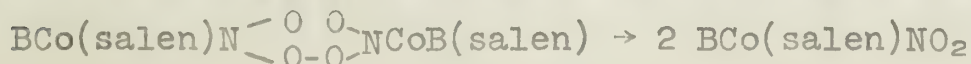
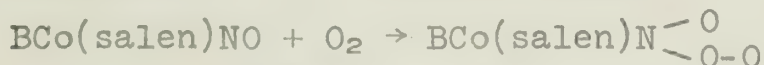
The bond angle cannot be determined by N-O infrared stretching frequency. The bent nitrosyls, with angles between 120° and 130° , have stretching frequencies between 1500 cm^{-1} and 1720 cm^{-1} . For the linear nitrosyls (170° to 180°), the stretching frequencies vary from 1600 cm^{-1} to 1950 cm^{-1} . The lack of correlation between N-O stretching frequency and bond angle, means that crystal structure is the only way to determine the M-N-O bond angle. Several attempts have been made to predict the bonding angle. They are based on the reducing power of the metal, charge of the complex, coordination number, other ligands present, molecular orbital calculations and symmetry.^{6,7,8,9}

The interest in the angle of the M-N-O bond arises because the two types react differently. The linear nitrosyl reacts like NO^+ and undergoes nucleophilic attack. An example of this is attack by hydroxide. The overall reaction uses two hydroxides and forms a nitrite. The proposed mechanism is:



Other nucleophilic attacks occur with N_3^- ,^{10,11} NH_3 ,¹² N_2H_4 ,^{12,13} Cr^{+2} ,¹⁴ Zn^{15} and H_2NAr .^{16,17}

Bent nitrosyls react like NO^- . An example of an electrophilic attack is dioxygen on $\text{Co}(\text{salen})\text{NO}$.¹⁸ The cobalt complex needs a base such as pyridine or phosphine in the sixth coordination site for dioxygen to react. The proposed mechanism is:

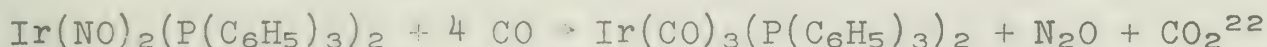


Other reactions of the bent nitrosyls are with NO,¹⁹ and H⁺.^{20,21}

An interesting reaction was first observed as:



This apparent substitution was unexpected since nitrosyls are not replaced by carbon monoxide. This is due to the strong M-N bond found in transition metal nitrosyls. As the reaction was studied, it was found that the other products were nitrous oxide and carbon dioxide. This meant the overall reaction was:



A recent study on a Rh analog found that water and acid increased the rate of reaction.²³ Due to environmental concerns over the production of nitric oxide, new nitrosyl complexes will be studied with the hope of finding an efficient catalyst for the decomposition of nitric oxide.

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John Breese

March 23, 1976

INTRODUCTION

During the past 20 years an increasingly large number of photochemical investigations of coordination complexes in solution have been reported.¹ However, in spite of this proliferation of photochemical studies of these species in solution, the photochemistry of solids has developed at a very slow rate. Although many reasons can be advanced for this slow development, including, until recently, a general lack of interest among inorganic photochemists, the major problem has been experimental. Thus, "although the inter- and intramolecular forces of an ordered periodic crystal lattice can be treated theoretically with considerably more certainty than the constantly changing conditions of fluid solutions, the analytical tasks, so necessary for solution of even simple reaction schemes, are unreasonably complicated because the rigid structures prevent facile separation of reactants and products."² However, because there are important fundamental concepts with roots in solid systems, the photochemistry of inorganic systems in the solid state is an area worthy of closer attention by Inorganic Chemists.

This discussion will be limited to the so-called "robust" coordination complexes, that is, complexes that maintain their coordination sphere when dissolved in fluid solution. The attempt will be to illustrate, from the small amount of data available, situations in the photochemistry of solids that are analogous to those of solutions and then to point out the properties of solids that can modify their behavior.

EXPERIMENTAL TECHNIQUES

When ligand field bands of a solid are photochemically excited, 99% of the light incident on the solid surface (assuming no reflection loss) is absorbed in a region 5-10 micrometers thick. If the excitement occurs in a charge-transfer region, the absorption layer is even thinner. It is the miniscule nature of this reaction zone that makes analysis of photoproducts very difficult and detection of reaction intermediates virtually impossible.

Two methods which are most popular for identifying and analyzing the photoproducts of coordination complexes have been the measurement of diffuse reflectance spectra³ and the infrared spectrum of materials dispersed in alkali halide pellets.⁴ Both techniques are well suited to the qualitative observation of the photochemistry of solids because they are sensitive to the changes on surfaces. Unfortunately, it is extremely tedious to calibrate these methods for the determination of quantum yields and therefore few such results appear in the literature.

The most common method used for the determination of quantum efficiencies for solid state reactions involves the use of reaction-rate plots from optical transmittance data for smooth layers or plates

of material (such as a pressed alkali halide pellet).⁵ The method combines the Beer-Lambert equation for light absorption with the appropriate reaction-rate equation. This gives an exact solution to the problem for the case in which the photoproducts are transparent. Unfortunately, for reactions of coordination complexes, the products often absorb as efficiently as the reactants. In this case, a similar treatment yields an approximate equation which is valid for short illumination time.⁶

PHOTOREACTIONS

The absorption spectra of solid coordination complexes are fundamentally the same as for the complexes in solution.⁷ There are, however, some differences in the subsequent thermal (or "dark") reactions as the emission spectra of some metal complexes (e.g., with Cr^{+3}) are different in the solid state than in solution.² Still, the photochemical reactions in solids are to a large extent similar to those that are observed in solution.^{8,9} That is, photosubstitution,¹⁰ charge-transfer photoredox,¹¹ and linkage isomerization¹² are observed in both solution and the solid state (photoracemization which is known to occur in solution has not yet been observed in the solid state). However, because of the rigidity of the solids and their periodicity, unusual adaptations of these reactions can be observed.¹³

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TRANSITION METAL CATALYZED REARRANGEMENTS OF POLYCYCLIC HYDROCARBONS

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In 1969, Woodward and Hoffman¹ published a classic review discussing the stereochemical pathways of concerted organic reactions. They postulated that the symmetry of the highest occupied molecular orbital of a molecule will be preserved throughout any concerted transformation. Thus, if the anti-bonding orbitals of the product are the only orbitals having the same symmetry as bonding orbitals in the reactants, a transition state of very high energy is likely to exist and the reaction is said to be "symmetry-forbidden." This simple application of basic molecular orbital theory to reaction chemistry has proven to be very accurate in predicting whether or not a given concerted reaction is likely to occur.

Recently, a large number of polycyclic hydrocarbons have been prepared. Although these molecules are often highly strained, they are quite stable because available rearrangement pathways are symmetry-forbidden. However, in the presence of many transition metal complexes strained polycyclic hydrocarbons are rapidly isomerized to thermodynamically more stable compounds.²⁻⁶

It has been proposed⁷ that the primary function of the transition metal in these isomerizations is to supply orbitals of the proper symmetry to accept electrons from the reactant and to donate electrons from orbitals of the proper symmetry to the product, thus allowing the concerted rearrangement to occur. However, recent work has shown that, depending on the catalyst, a variety of non-concerted mechanisms for these rearrangements may exist.

In the presence of Ag^+ cubane(1) isomerizes to cuneane(2).⁸ Similarly, bishomocubane(3) isomerizes to snoutane(4). Detailed



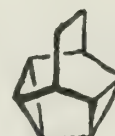
(1)



(2)



(3)



(4)



(5)

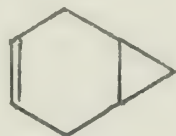


(6)

kinetic and mechanistic studies⁹⁻¹¹ of the isomerizations of substituted derivatives of the bishomocubane and homocubane systems indicate that the initial step in these rearrangements is electrophilic attack by Ag^+ on an edge of the molecule. This gives rise to a delocalized cyclopropylcarbinyl cation which releases Ag^+ giving the final product.

When PdCl_2 is used as a catalyst, the same products are obtained as in the presence of Ag^+ .⁸ However, with complexes of the type PdR_2Cl_2 , where R is a ligand with weak σ donor and strong π acceptor capabilities, a mixture of snoutane(4) and tricyclodecadiene(5) is obtained from bishomocubane.¹²⁻¹⁴ When R is a ligand with a strong σ donor and strong π acceptor capabilities, isomerization to the diene is the favored process. The amount of diene produced correlates well with the ability of the palladium complex to undergo oxidative addition.¹⁵ Furthermore, in the presence of complexes of the type $\text{Rh}(\text{diene})\text{Cl}/_2$ cubane (1) is quantitatively converted into tricyclo-octadiene(6).¹⁶ When $\text{Rh}(\text{CO})_2\text{Cl}/_2$ is used, an acylrhodium complex can be isolated which must arise from the oxidative addition of a carbon-carbon σ bond, followed by CO insertion. These results imply that the isomerizations can proceed through oxidative addition of a strained carbon-carbon bond followed by rearrangement and reductive elimination to give the final product.

Finally, it has been shown that for some PdII complexes another mechanistic pathway may be operative. Cis-bicyclo[6.1.0] non-4-ene(7) is isomerized to 1,5-cyclononadiene(8) by $\text{PdCl}_2(\text{PhCN})_2$.¹⁷ This process has been shown to proceed through chloropalladation of the cyclopropane ring, followed by 1,2-hydrogen migration and elimination of PdCl to give the nonadiene product. It remains to be seen if this type of rearrangement pathway is also applicable to the isomerizations of the cubane derivatives.



(7)



(8)

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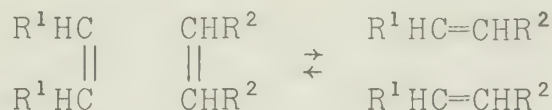
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SOME ASPECTS OF THE OLEFIN METATHESIS REACTION

William Willis

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The metal catalyzed olefin metathesis reaction, first reported by Banks and Bailey¹ in 1964, can be formally represented as follows:



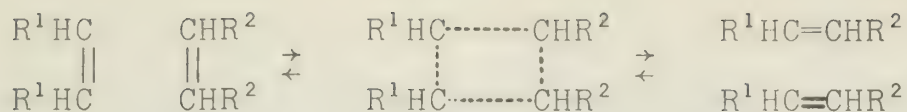
Other workers, employing ²H and ¹⁴C labeling,^{3,4} confirmed the complete breaking of olefinic bonds, and the formation of new olefinic bonds, as shown above. This reaction proved to be of industrial importance⁵ (e.g., Phillips Triolefin process for propylene matathesis) and of theoretical interest. This discussion will concern the nature of metathesis catalysts, the kinds of products obtained, and several proposed intermediates involved in the reaction.

The most effective heterogeneous catalysts are generally oxides or carbonyls of W or Mo, usually supported on refractory materials such as SiO₂ or Al₂O₃. Other metal compounds, e.g., Re₂O₇ can act as catalysts, but are much less effective. The function of the promoter (transition metal compound) and support are not clearly divided; changing the support will often alter the effectiveness of the catalyst. Reactions are usually run at elevated temperature (150° - 500°C)⁵.

Most homogeneous catalysts consist of a transition metal compound and a non-transition metal co-catalyst, often aluminum alkyl halides, lithium alkyls, and Grignard reagents. Halides and carbonyls of W and nitrosyls of Mo are most effective transition metal constituents. Some systems employ an alcohol as a third component of the catalytic mixture.⁵ It is not clear whether or not the so-called homogeneous systems are actually homogeneous. The WCl₆/EtAlCl₂/EtOH mixture has been debated in this regard.⁶⁻⁸ Reactions are usually run at room temperature, and may or may not use diluents (e.g., alkanes or aromatic compounds).

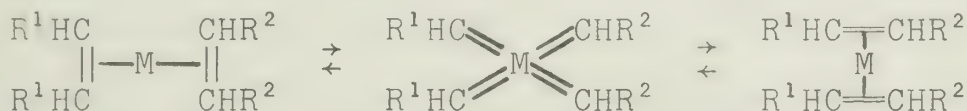
Most olefin metathesis systems have several notable features: (1) Reactions are athermal, i.e., ΔH~0. (2) Equilibrium is readily achieved by using either starting materials or products, i.e., the reaction is reversible. (3) The kinds of products obtainable can be predicted by random pairing of all available alkylidene groups. (4) The concentrations of reactants and products appear to be determined by entropic and stereochemical factors.^{2,5} Side reactions, such as double bond isomerization, also occur. The multi-component nature of the catalysts, the complexity of product mixtures, and the failure to identify the catalytically active species have hampered progress in determining the reaction mechanism. In some cases, the concentration of catalyst required to rapidly reach equilibrium may be very small, indicating a very labile intermediate.

While detailed mechanistic information is lacking, several intermediates have been proposed to adduce the nature and distribution of products. The first mechanism suggested the initial coordination of two olefins to the metal center, followed by a concerted [2+2] cycloaddition reaction for the formation of a "quasicyclobutane" intermediate:



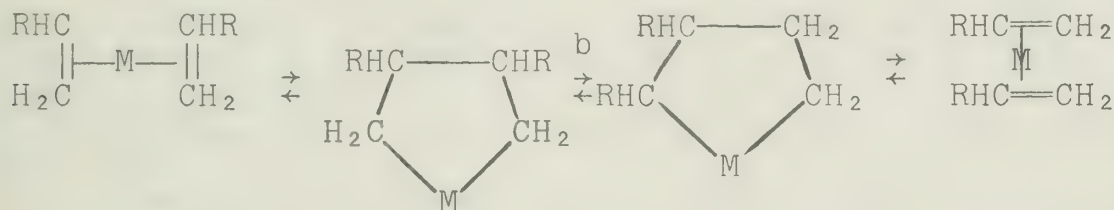
The uncatalyzed reaction is thermally forbidden. Several articles have appeared concerning this problem. Each invokes an electron transfer through available d orbitals to remove the forbiddenness of the reaction.¹⁰ A more detailed theoretical approach has raised questions concerning the allowedness of quasicyclobutane formation in the case of d^{2-10} metal systems. Another problem is the lack of cyclobutane formation in all catalytic systems reported to date, and the nonreactivity of free cyclobutanes with catalyst systems.¹¹

Later workers proposed an intermediate containing no antisymmetric ligand orbitals, thus circumventing symmetry restrictions.¹² In their model, the initially coordinated olefins split into four separate carbene ligands. The carbene ligands then join to form new olefins.



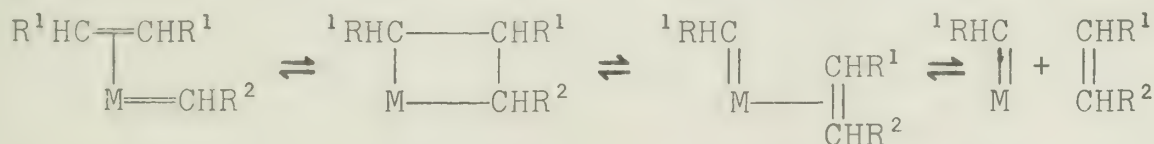
It was later recognized that catalysts derived from $\text{W}(\text{CO})_6$ could have only two CO ligands coordinated to the metal under these conditions, due to coordinate saturation of the metal.¹³ Experimental evidence does not conclusively rule out this intermediate, however.

A third mechanism requires the formation of a 5-membered metallocycle.¹⁴ The authors do not propose a pathway for step b.

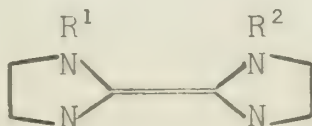


This mechanism was based on the reaction of 1,4-dilithiobutane with WCl_6 , which resulted in the formation of ethylene.

A fourth mechanism has been proposed in which a carbene and a coordinated olefin form a 4-membered metallocycle:



Attack by $\text{R}^2\text{HC}=\text{CHR}^2$ on the last species results in the formation of more mixed alkylidene product $\text{R}^1\text{HC}=\text{CHR}^2$. Several papers have appeared giving evidence for the intermediacy of coordinated carbenes.¹⁵⁻¹⁸ This has been demonstrated in particular by the isolation of catalytically active carbene intermediates which result from the reaction of $\text{L}(\text{PH}_3\text{P})_2$ RhCl and



CONCLUSION

The mechanism of the olefin metathesis reaction remains unsolved, and will require further investigation of simpler catalytic systems from which active intermediates can be isolated, or otherwise identified. Of the several proposed pathways, the 4-membered metallocycle mechanism appears to present the fewest difficulties, and should provide additional direction for future work.

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ONE DIMENSIONAL METALLIC CONDUCTORS DERIVED FROM THIRD ROW

d^8 TRANSITION METAL COMPLEXES

Anton Elamma

April 20, 1976

In the solid state, the partially oxidized complexes of Pt(II) and Ir(I) are one-dimensional (1-D) electronic conductors.^{1,2,3,4} These compounds form parallel linear chains^{5,6,7} and have short metal-metal bonds like those in pure metals. Unoxidized complexes such as $K_2Pt(CN)_4$ also form linear chains⁸ in which extensive Pt-Pt interactions exist but are not electronic conductors. It has been suggested⁹ that the interactions of primary concern involve the d_{z^2} orbitals on the metal centers which overlap in the solid state to form a valence band of appreciable width. The energy level of d_{z^2} in $[Pt(CN)_4]^-$ is still debatable;¹⁰ nevertheless, the upper levels² of the valence band are antibonding. The removal of electrons from this part of the band by partial oxidation strengthens the bonding in the chain and forms a partially filled band which by definition is metallic.

The partially oxidized phase $K_2[Pt(CN)_4]Br_{0.30}.nH_2O(KCP)$ has optical properties similar to metals¹¹ and a room temperature conductivity² $\sigma \cong 300 \text{ ohm}^{-1} \text{ cm}^{-1}$. This simple picture does not account for the smooth decline of the conductivity with decreasing temperature leading to an insulator at 20°K, $\sigma = 10^{-12} \text{ ohm}^{-1} \text{ cm}^{-1}$.

Peierls¹² has shown that, in the absence of electron-lattice vibration interactions, a 1-D metal is an unstable structure. It undergoes a spontaneous lattice distortion which by the creation of an energy gap at the Fermi level splits the metallic band into filled and empty bands. Consequently, the energy of the system is lowered, and a 1-D metal becomes an intrinsic semiconductor or an insulator. The Peierls' distortion is described using the arguments of Tight-Binding-Band-Theory, which is the LCAO approach for crystalline solids.¹³

The phonon spectrum¹⁴ of KCP using neutron scattering techniques shows a Kohn¹⁵ anomaly. A Kohn anomaly arises from the interaction of lattice vibrations (phonons) with electrons. The phonons are quantized and each has an assigned wave vector $q = 2\pi/\lambda$ (λ is the wavelength of the phonon). The lattice favors the phonons which enhance the manifestation of a Peierls' distortion since this lowers the total kinetic energy of the electrons. When the harmonic restoring forces in the lattice no longer have sufficient thermal energy to return the atoms or molecules to the undistorted equilibrium configuration, the energy associated with the Peierls' effect dominates and a metal-insulator transition takes place.

The features necessary for 1-D conducting systems are discussed. Synthetic routes^{16,17,18} and conductivity-measurement techniques¹⁹ are described for the partially oxidized phases.

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THERMODYNAMIC AND SPECTROSCOPIC STUDIES OF REACTIVITY AND BONDING IN TRANSITION METAL LEWIS ACID-BASE SYSTEMS

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(Final Seminar)

April 22, 1976

Introduction

Spurred by the growing concern with homogeneous catalysis, the reactivity and bonding of organometallic complexes of Group VIII metals having a d^8 configuration have been the subject of widespread attention^{1,2} among inorganic chemists during this past decade. In many of these catalytic systems, it is felt that a critical step in the mechanism involves coordination of the substrate to the metal, which can be viewed as a Lewis acid-base interaction. Thus, our initial approach to understanding the behavior of such heavy metal systems in catalysis was to obtain quantitative knowledge of the Lewis acidity of dimeric rhodium(I) and palladium(II) systems in their behavior towards a variety of Lewis bases. The elucidation of factors affecting the strength of interaction may aid in the future design of catalytic systems. As yet, the quantitative effects of introducing a second metal complex into the coordination sphere of a first metal center remain relatively unexplored. Only when concepts of reaction mechanisms are developed to a point where one can predict with confidence new syntheses which can be put into experimental practice, will the field of homogeneous catalysis by organometallic compounds have acquired a more rational than empirical basis.

Comparison of Acid-Base Parameters and Bridge Cleavage Energies for Heavy Metal Dimers

Analogous bridge-splitting reactions have been reported for a variety of Lewis bases reacting with the chloro-bridged dimers $[\text{Rh}(1,5\text{-cyclooctadiene})\text{Cl}]_2$,³ $[\text{Rh}(\text{CO})_2\text{Cl}]_2$,⁴ and $\text{Pd}(\pi\text{-methylallyl})\text{-Cl}]_2$.⁵ It is of interest to examine the effects of changing the metal and its oxidation state as well as the terminal substituents on the calorimetrically measured enthalpies of adduct formation for these heavy metal dimers. A quantitative comparison of acid-base parameters and bridge cleavage energies for these three systems is made.

Development and Tests of a Proposed Acid-Base Model for Mixed Metal Dimer Formation

One can show that when the C_A/E_A ratios of a series of acids are similar, the E and C equation⁶ can be converted from a double-scale enthalpy equation to a single-scale enthalpy relation.

$$-\Delta H = E_A P_B \quad (1)$$

$$\text{where } P_B = E_B + \left(\frac{C_A}{E_A} \right) C_B \quad (2)$$

Knowing the energies required to dissociate the symmetrical dimers and the E_A and P_B parameters describing the acidity and basicity of the monomeric acids and chloride bridges respectively, one is in a position to predict the net enthalpy expected for the reaction of mixing two symmetrical dimers to form an unsymmetrical mixed dimer species. 1H nmr, $^{13}C\{^1H\}$ nmr, and infrared spectroscopy are employed to investigate the formation of certain mixed dimers and to test our predictions for mixed dimer formation.

From this research, a general guideline for the design and synthesis of mixed dimers has emerged. In general, for any case where the C/E ratios for the two metal centers is similar and the P_B value of the bridging ligands comparable, there will be no net enthalpic driving force for forming the mixed dimer regardless of the acid strength of the two metal centers or the relative values of C_B and E_B which lead to the same P_B . In order to maximize the enthalpic driving force for forming any mixed dimer system, it is necessary to increase the P_B parameter of the bridging atom(s) on the less acidic center and decrease the P_B parameter of the bridging ligand on the more acidic center. Once again, the obvious value of quantitative assessments of acid and base parameters for various systems is apparent.

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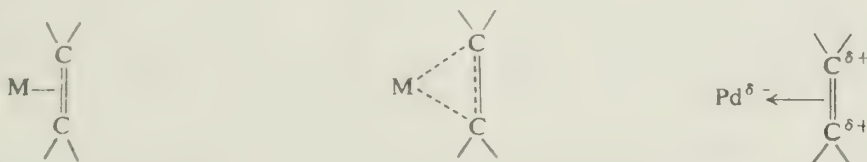
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ADDITION OF NUCLEOPHILES TO COORDINATED OLEFINS

Dennis Sepelak

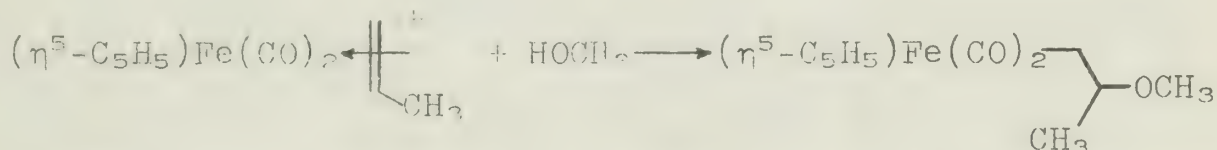
April 27, 1976

Although addition of electrophiles to olefins occurs easily, addition of nucleophiles only occurs when the double bond is activated by the presence of electron withdrawing substituents. Creation of a partial positive charge by inductive or resonance effects is necessary to allow attack by the nucleophile on the electron rich alkene.¹ Complexation by a transition metal alters the bonding in an olefin and can activate the double bond toward attack. A low valent metal can increase susceptibility toward electrophilic additions, whereas an olefin-metal complex with the metal in a higher oxidation state (e.g., Pd(II)) facilitates attack on the olefin by nucleophiles.² This is a result of partial withdrawal of electron density from the double bond by the positively charged metal.^{3,4}



Although stable metal-olefin π complexes are known for most of the transition metals from the chromium subgroup to the copper subgroup,⁵ most of the work involving addition of nucleophiles to coordinated olefins has been done with Pd(II), Pt(II), and Fe(II) (as the $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{alkene}]^+$ complexes). Palladium(II) olefin complexes undergo the greatest variety of nucleophilic additions, both stoichiometric and catalytic.^{6,7,8,9}

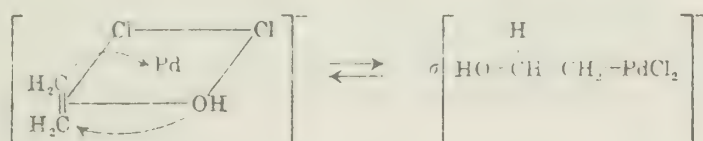
Olefin complexes of the $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2^+$ ion can be prepared in a number of ways, including protonation of the η^1 -allyl compounds and σ -hydride abstraction from $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ alkyls. However, for synthetic purposes, olefin exchange with the $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{isobutylene})^+$ cation and the reaction of $\text{Na}(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ with epoxides are probably most useful.¹⁰ The latter reaction occurs with retention of configuration.¹¹ These complexes undergo addition by alcohols, amines, enamines, cyanide and phosphines as well as anionic nucleophiles such as enolate anions. The reactions are frequently regiospecific.^{12,13} Reactions of similar complexes of other metals have been studied.¹⁴



Olefin complexes of palladium(II) can be formed by simply adding olefins to solutions of Pd(II) salts, such as $[\text{PdCl}_4]^{2-}$.⁵ It was known for quite some time that palladium-ethylene complexes undergo stoichiometric reaction with water to yield acetaldehyde and palladium metal.¹⁵ However, it was not until J. Schmidt and coworkers at

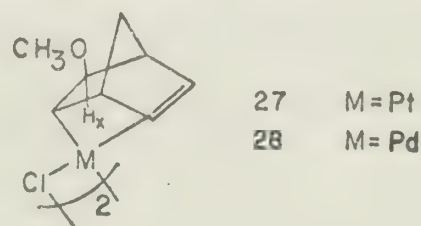
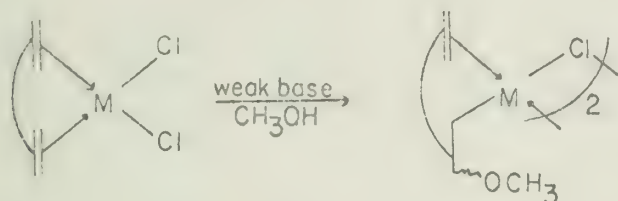
Wacker Chemie¹⁶ observed that the palladium could be oxidized back to Pd(II) by such agents as Cu(II) (which could in turn be oxidized by atmospheric oxygen) that extensive work was done in this area.

Elucidating the kinetics and mechanism of the olefin oxidation reaction was the object of much work by a number of workers.^{17,18,19} The evidence suggests a mechanism in which there is nucleophilic attack by a coordinated hydroxo group cis to the olefin.



Since the discovery of the Wacker process, addition of a variety of nucleophiles has been observed, including alcohols,²⁰ amines,²¹ enolate anions, carboxylic acids,²² arenes,²³ and chloride ion. Reactions also occur with dienes, allenes, and butadienes.

The stereochemistry of the addition to dienes and bidentate olefins was found to be trans, indicating addition of noncoordinating nucleophiles.²⁴



Trans addition was also found to be the case in reactions of monoolefins with alcohols,²⁵ acetate,²⁶ and amines.²⁷ Additions in which the nucleophile is coordinated to the metal prior to reaction appear to occur through anti-Markownikoff cis addition and elimination, whereas addition of noncoordinated nucleophiles is Markownikoff with trans addition and elimination.²⁵

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INORGANIC CHEMISTRY IN THE GAS PHASE AS REVEALED BY ION CYCLOTRON RESONANCE SPECTROSCOPY¹

Patrick Cannady

May 4, 1976

INTRODUCTION

The motion of an ion in a uniform magnetic field is restricted to a circular orbit in a plane perpendicular to the direction of the field. Electromagnetic energy of a frequency equal to the cyclotron frequency, ω_c ,

$$\omega_c = \frac{qH}{mc}$$

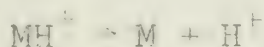
is absorbed by such ions, and the absorption of power detected by a marginal oscillator detector. With the observing frequency held constant, sweeping the magnetic field yields a spectrum linear in mass. This is known as the single resonance spectrum, and at high electron ionizing energies (~ 70 eV) yields the mass spectrum of the sample.

By varying the electron energy, appearance potentials can be determined and reactions of primary and secondary ions with the parent neutral species at various pressures can be investigated. The technique of double resonance as applied to ion cyclotron resonance (icr)^{2,3} allows for the unequivocal identification of reaction pathways for these ion-molecule reactions. In this technique, a second radio-frequency field is swept as the first radiofrequency field and the magnetic field are held at resonance conditions for the product ion under study. As the second RF field comes into resonance with the precursor ions, the energy absorbed will cause a change in the reaction rate, altering the rate of product ion observation, thus identifying the precursors of the product ion.

Trapped ion techniques,⁴ in which ions produced by electron impact are held in the source region by an electromagnetic force field for a desired period of time before detection, allow for direct observation of the time dependence of product distributions and abundances. The extraction of kinetic parameters is thus greatly simplified.

APPLICATIONS

Ion-molecule reactions in the gas phase are rather conveniently investigated by icr methods. Gas phase Lewis acidities and basicities of a number of inorganic hydrides as well as those of small organic molecules have been and continue to be investigated. Gas phase basicities are characterized by the proton affinity (PA), which is defined as the enthalpy change of the reaction



and by the hydrogen affinity (HA), or, as it is often referred to, the homolytic bond dissociation energy, $D(M^{\cdot+}-H)$, which is the enthalpy

change of the reaction



These two quantities are related by the ionization potential of M, by the equation

$$\text{PA}(\text{M}) - \text{D}(\text{M}^+-\text{H}) = \text{IP}(\text{H}) - \text{IP}(\text{M})$$

Within a homologous series, the hydrogen affinity is usually found to be a constant, resulting in a direct parallel between the proton affinity and the ionization potential of the base. Thus, the order of basicities in such a series follows the order of the inductive electron donating abilities of the substituents. For example, the proton affinities of the methyl amines increases in the order $\text{PA}(\text{H}_2\text{NCH}_3) < \text{PA}(\text{HN}(\text{CH}_3)_2) < \text{PA}(\text{N}(\text{CH}_3)_3)$ in the gas phase. In contrast, solution basicities yield an inverted order, $\text{PA}(\text{H}_2\text{NCH}_3) < \text{PA}(\text{HN}(\text{CH}_3)_2) < \text{PA}(\text{N}(\text{CH}_3)_3)$. The inverted order is due to complicating solvent effects, which are totally lacking in the gas phase.⁵

Acidities can be measured in terms of other ion affinities than proton affinities. Inorganic anions such as F^- have been used to determine Lewis acidities in the gas phase of some inorganic fluorides.⁶ Relative F^- ion affinities ($\text{IA} = \Delta\text{H}$ for the reaction: $\text{AX}^-(\text{g}) \rightarrow \text{A}(\text{g}) + \text{X}^-(\text{g})$) are found to increase in the order SF_4 , SF_5^- , SO_2 , AsF_3 < SiF_4 < BF_3 < PF_5 < BCl_3 < AsF_5 , which is in agreement with earlier solution work done in CH_2Cl_2 .⁷

Proton affinities and hydrogen affinities have been measured in the gas phase for such organometallic species as $\text{Fe}(\text{CO})_5$, $\text{Fe}(\text{C}_5\text{H}_5)_2$, and $\text{Ni}(\text{C}_5\text{H}_5)_2$ and are summarized below:^{8,9,10}

	<u>PA</u>	<u>HA</u>
$\text{Fe}(\text{CO})_5$	198 kcal/mol	74 ₊₃ kcal/mol
$\text{Fe}(\text{C}_5\text{H}_5)_2$	207 kcal/mol	56.6 ₊₆ kcal/mol
$\text{Ni}(\text{C}_5\text{H}_5)_2$	218.9 kcal/mol	48.3 ₊₃ kcal/mol

The positive ion chemistry of $\text{Fe}(\text{CO})_5$ ^{9,10,11} is quite rich, with evidence found for the formation of polynuclear $\text{Fe}_x(\text{CO})_n^+$ ions, where x ranges from 2 to 4, and n from 3 to 12. Higher polynuclear species are postulated, but as yet an upper limit of m/e=600 cannot be exceeded with present experimental configurations. Ligand displacement reactions between $\text{Fe}(\text{CO})_5^+$ (n=1-5) have been investigated for a series of ligands. $\text{Fe}(\text{CO})_5$ itself is found to be rather inert to substitution, whereas $\text{Fe}(\text{CO})_3$ is most active. The gas phase basicities of the $\text{Fe}(\text{CO})_5$, $\text{Fe}(\text{C}_5\text{H}_5)_2$, and $\text{Ni}(\text{C}_5\text{H}_5)_2$ species are rather large ($\text{PA}(\text{NH}_3) = 201$ kcal/mol). $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{C}_5\text{H}_5)_2$ are known to protonate only in highly acidic solutions, with proton-metal bonds being formed. Studies⁸ have been directed towards discerning the site of protonation of $\text{Fe}(\text{C}_5\text{H}_5)_2$ and $\text{Ni}(\text{C}_5\text{H}_5)_2$ in the gas phase, but the results are as yet inconclusive. The negative ion chemistry of $\text{Ni}(\text{CO})_4$ and $\text{Cr}(\text{CO})_6$ has also been investigated and is dominated by the formation of binuclear metal complexes.

CONCLUSION

ICR spectroscopy has tremendous potential as a tool for the investigation of certain intrinsic aspects of organometallic chemistry in the gas phase, in the absence of complicating solvent phenomena. Areas of particular interest may be: (1) polynuclear metal cluster formation, (2) ligand substitution processes, (3) relative ligand binding energy determinations, (4) transition metal basicities, (5) processes involving both electrophilic and nucleophilic attack on neutral metal complexes, (6) unusual σ - and π -bonded organometallic complexes, and (7) photochemistry of gaseous organometallic compounds.

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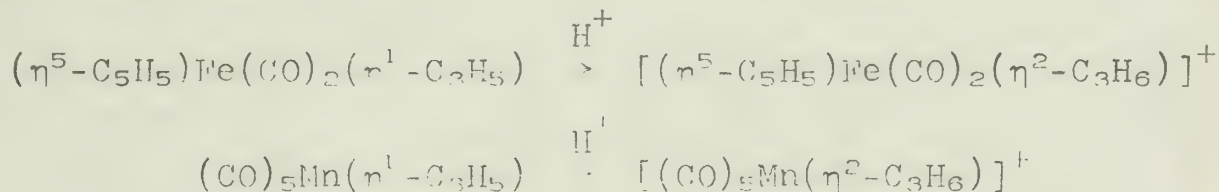
SIGMA-PI REARRANGEMENTS IN ORGANOMETALLIC SYSTEMS

Keith Hodges

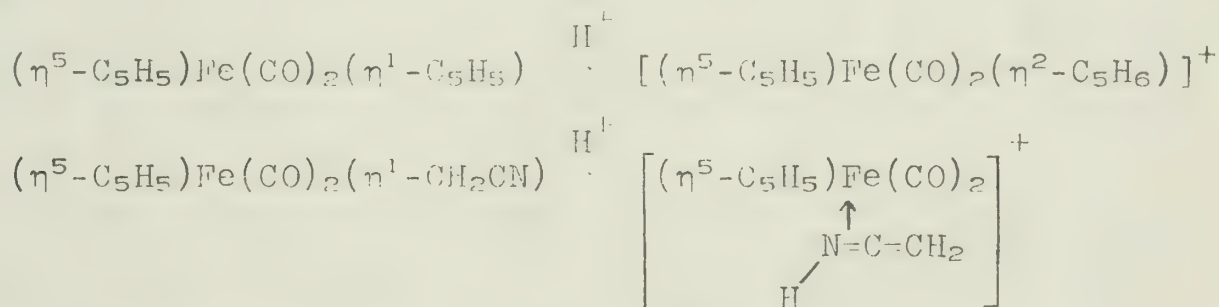
May 11, 1976

In 1957 it was first recognized that an organic group σ -bonded to a transition metal could rearrange to a π -bonded species. This discovery came with the elucidation of the structures of bisbiphenyl chromium(0) and benzene biphenyl chromium(0)' (Hein's complexes) and the isolation of the intermediate in their preparation, tri- σ -phenyl chromium tristetrahydrofuranate.² Since then these rearrangements have been observed for a wide variety of organometallic compounds and several industrially important processes rely on reactions involving σ - π rearrangements; most notably, the Ziegler-Natta process for the polymerization of olefins, the Wacker process for the oxidation of ethylene to acetaldehyde, and the "oxo" process for the hydroformylation of olefins.

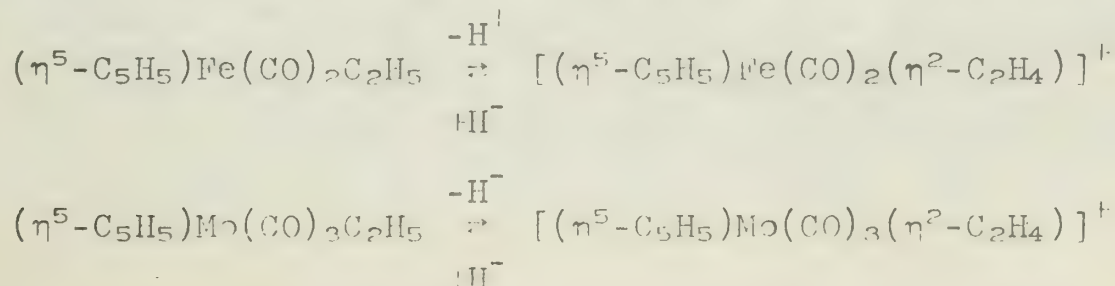
Sigma-pi rearrangements (and the converse, pi-sigma rearrangements) are intramolecular processes that can be classified in two general categories. The first classification involves reactions of the organic moiety that induce rearrangement. For example, many σ -bonded allyl complexes are readily protonated by mineral acids to give the corresponding π -propene cationic complexes. Specific examples include:^{3,4}



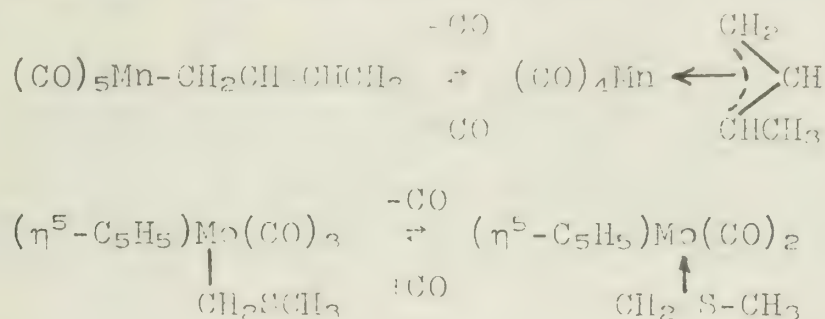
Such reactions are not limited to allyl complexes, however, and have been observed for numerous unsaturated organic groups bound to a metal, e.g.,^{5,6}



Alternatively, abstraction of a hydride ion from the organic group of a metal-alkyl complex can generate a cationic π -alkene complex. Interestingly, this reaction is often reversed on the addition of NaBH_4 .^{7,8}



The second classification of sigma-pi rearrangements involves the addition or abstraction of ligands bound to the metal to induce a coordination change in the organic group. Some reactions are reversible, and the most numerous examples exist for carbonyl complexes. Fe,⁹ Mn,¹⁰ Mo¹¹ and W¹² carbonyls with σ -bound organic substituents rearrange to the corresponding π -complex upon loss of CO, e.g.,



Analogous reactions have been observed in cobalt cyanide complexes. The σ -butenyl complex obtained by the addition of butadiene to hydrido-pentacyanocobaltate(III) can eliminate cyanide ion to give a π -butenyl complex.¹³ Similar steps have been proposed in the mechanism of the stereoselective hydrogenation of butadiene by pentacyanocobaltate(II) in the presence of H₂.¹⁴

Attempts have been made to show that addition or elimination of ligands and concomitant rearrangements are a function of the π -bonding strength of the ancillary ligands in the complex. For σ -bonded compounds a correlation has been drawn between their stability and the possibility of electronic transitions from high energy filled d orbitals into the lowest antibonding molecular orbitals corresponding to the first step in metal-carbon bond rupture.¹⁵ Increasing the energy of this transition (ΔE) by the addition of ligands which stabilize the nonbonding d orbitals should result in a more stable σ -complex. In π -complexes, ΔE is increased by the interaction of the metal d orbitals and the antibonding π -orbitals of the organic group. Thus the σ -state will be destabilized with respect to the π -state on losing a ligand and a σ - π rearrangement can occur. The reverse can occur upon addition of a strong π -bonding ligand to a π -complex. This leads one to predict that addition of ligands such as CO, CN, PR₃ and DMSO to π -complexes should result in pi-sigma rearrangements.

CONCLUSIONS: This area of study provides a fertile ground for research into catalytic systems, the activation of C-H bonds and the preparation of inherently unstable organic molecules that are difficult or impossible to prepare by conventional routes.

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INVESTIGATIONS INTO THE ELECTRONIC STRUCTURE OF DIOXYGEN COORDINATED TO COBALT(II) COMPLEXES

David J. Kitko

(Final Thesis)

May 25, 1976

Introduction

The reversible binding of molecular oxygen to transition metal complexes has been an active area of research for many years. In 1947, Calvin and Bailes reported on their extensive investigations of dioxygen binding to a series of tetradentate Schiff-base complexes of Co(II) in the solid state.¹ Since that time, a variety of ligand environments surrounding a Co(II) ion has been shown to lead to reversible binding of dioxygen. More recently, the research in this area has been motivated by a desire to elucidate the factors influencing the binding of O₂ in biological systems, and to understand the mechanisms of the highly selective oxidations carried out with O₂ in some of these systems. Our primary interest in this area has been the activation of O₂ in the oxidations of organic substrates, particularly olefins. It was felt that by coordinating dioxygen to a transition metal center, it would be possible to overcome some of its kinetic inertness, and perhaps obtain some degree of selectivity in the oxidation. As basic information, we thought it necessary to determine the net perturbation made on dioxygen upon coordination. The Co(II) complexes were ideal for this study as they, in general, result in O₂ adducts with one unpaired electron making them suitable for study via ESR. A great deal of research had previously been done on O₂ adducts of Co(II), and these studies led to their characterization as Co(III)·O₂⁻.² For a number of reasons, it was felt that this characterization, although correct in the formal sense, did not provide a true description of the perturbation made on the O₂ fragment upon coordination. In an attempt to clarify this problem and to gain some additional information concerning the stability of the O₂ adducts, the following studies were conducted.

Results and Discussion

Earlier studies had indicated that Co(SALMeDPT), a neutral penta-coordinate Schiff-base complex, reversibly bound O₂ in solution at low temperatures.³ However, attempts to use this complex in the catalytic oxidation of a variety of olefinic substrates failed. Systematic variations in the ligand framework were then implemented. The N-CH₃ group was replaced by an etheral oxygen donor, -O-, and thioether donor, -S-, and substituents were added to the aromatic rings. As a final perturbation, the salicylaldehyde portion of the Schiff-base ligand was replaced by the β-ketoamino structure through the condensation of the primary amines with acetylacetone and benzoylacetone.

The reactivity of these complexes towards Lewis bases and towards O₂ was then investigated using ESR and UV-visible spectroscopy. Low spin adducts formed between all of these complexes and strong π-back-bonding Lewis bases, and were characterized by ESR. The Co(X-SALDAPE) and Co(acac₂MDPT) complexes also reversibly bound O₂. The O₂ adducts were also characterized by ESR in frozen toluene/CH₂Cl₂ solution. The very large cobalt hyperfine parameters found for the adducts of Co(X-SALDAPE) series coupled with a report of the anisotropic ¹⁷O hyperfine in the ESR spectrum of Co(bzacen)py¹⁷O₂⁴ led to a qualitative molecular orbital scheme to explain the bonding between Co and the O₂

fragment. This model predicted that the unpaired electron will reside on the O_2 fragment regardless of the extent of electron transfer from Co to O_2 . A detailed analysis of the anisotropic cobalt hyperfine, using a spin polarization analysis similar to that employed elsewhere by Raynor⁵ and Symons,⁶ has led to an estimate of the extent of electron transfer from Co to O_2 upon adduct formation. The extent of electron transfer roughly parallels the strength of the donor atom set surrounding cobalt.⁷

A KINETIC STUDY OF A METAL ION COORDINATION SPHERE EXCHANGE REACTION

In recent years, there has been a growing interest in polynuclear transition metal complexes. This research has been spurred by a desire to obtain fundamental information about two very important areas, metalloenzymes and heterogeneous catalysis. The general thrust of these research efforts has been to prepare simpler compounds which model in structure and/or reactivity of the active site of the *in vivo* metallo-enzyme or the active site of a heterogeneous catalyst. Our research in this area has been motivated by a desire to determine and attempt to understand the effect of one metal center on the chemistry (reactivity and physical properties) of the second metal center within the polynuclear compound. O'Bryan has recently prepared and characterized a series of binuclear complexes of the type $M(\text{salen})M'(\text{hfac})_2$.⁸ In the process of characterizing these compounds, it was discovered that the binuclear complex $\text{Cu}(\text{salen})\text{Co}(\text{hfac})_2$ could be prepared by the direct reaction of $\text{Cu}(\text{salen})$ with $\text{Co}(\text{hfac})_2 \cdot 2\text{H}_2\text{O}$ or by a ligand interchange process using $\text{Co}(\text{salen})$ and $\text{Cu}(\text{hfac})_2$, equation 1.

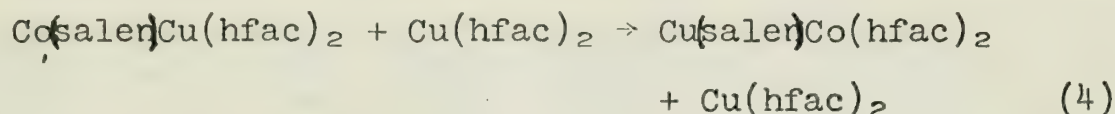
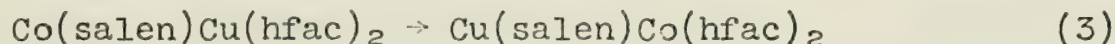
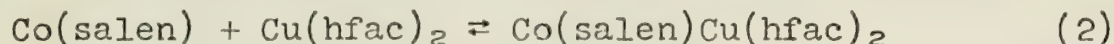


The latter reaction was very rapid at 25°C in dilute CH_2Cl_2 solution. This result was intriguing and unexpected in this solvent medium where ligand dissociation and the generation coordinatively unsaturated ionic species is regarded as highly unlikely. Information about the mechanism of this unique metal ion-coordination sphere exchange process was considered necessary in attempting to understand the chemistry of this class of binuclear complexes. A detailed kinetic investigation of this reaction was therefore conducted using stopped-flow, UV-visible spectroscopy.

Results and Discussion

The kinetics of the reaction between $\text{Co}(\text{salen})$ and $\text{Cu}(\text{hfac})_2$ in CH_2Cl_2 at 25°C were studied with $\text{Cu}(\text{hfac})_2$ present in 3- to 80-fold excess. The reaction was monitored at 470nm, which corresponds to a flat region in the visible spectrum of $\text{Co}(\text{salen})$ and a minimum in the $\text{Cu}(\text{hfac})_2$ spectrum. Even under conditions of ca. 80-fold excess of $\text{Cu}(\text{hfac})_2$, the overall reaction does not exhibit pseudo-first-order kinetic behavior. The kinetic curves indicate the very rapid formation of an intermediate, which proceeds to product at a much slower rate. Rate studies at low $\text{Co}(\text{salen})$ and $\text{Cu}(\text{hfac})_2$ concentrations indicate that the intermediate is generated by a second-order process, first-order in each reactant. The further reaction of the intermediate appears to be catalyzed by $\text{Cu}(\text{hfac})_2$. The rate of disappearance of the intermediate was subjected to a pseudo-first-order kinetic treatment. A

plot of k_{obs} vs. $\text{Cu}(\text{hfac})_2$ concentration yields a straight line with slope = $23 \text{ M}^{-1} \text{ sec}^{-1}$ and intercept = 0.53 sec^{-1} . This information suggested the following mechanism for the reaction.



In order to verify the suitability of this mechanism, the PLATO IV computer system was used to calculate theoretical curves of $\%T$ vs. time via numerical integration of the differential equations corresponding to a proposed mechanism. Plots of experimental data were superimposed upon the calculated curves in order to estimate the accuracy of the fit.

It was possible to fit the kinetic curves for a wide range of concentrations of reactants with the mechanism represented by equations 2-4. Further kinetic and visible spectroscopic studies lend support to a mechanism in which the coordination sphere exchange process occurs without dissociation of a ligand, and indicates that initial adduct formation is required before the exchange will occur.

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TEMPERATURE DEPENDENT STUDIES OF STRUCTURAL AND ELECTRONIC
EFFECTS IN SINGLE CRYSTALS

Gerald Delker

(Final Seminar)

May 28, 1976

The solid state properties of two transition metal systems which exhibit magnetic moments that change abruptly as a function of temperature are reported. The first system is the octahedral complex tris(4-((6-methyl)-2-pyridyl)-3-aza-3-butenyl)amino iron(II) hexafluorophosphate, which exhibits a sharp change in magnetic moment from high-spin to low-spin near 215°K in the solid state. In order to investigate this transition, the single crystal x-ray structure, I.R. spectra and the visible spectra were determined both above and below the transition. The Fe-N bond lengths determined for the 295°K crystal structure are consistent for an iron atom in the high-spin configuration, while at 80°K, a decrease in the Fe-N bond lengths of 0.17Å is observed which is consistent for a low-spin structure. The I.R. and visible spectra are observed to change as a function of temperature, with the I.R. spectra reflecting the changes in the Fe-N and N=C vibrations agreeing with a change in bond strengths. To investigate the effect that an anion might have on the magnetic susceptibility, the complex was prepared using tetrafluoroborate, tetraphenylborate, bromide, and iodide anions. The magnetic susceptibility, I.R. and visible spectra were investigated for each of these complexes, and compared with the hexafluorophosphate complex. It is observed that the size of the anion has an effect on the spin transition, such that for larger anions, and for complexes which have solvent molecules trapped in the lattice, the complex remains high-spin, or has only a slight decrease in magnetic susceptibility, while for smaller anions, the complex is low-spin at room temperature. These results are discussed in terms of intermolecular interactions via phonon coupling to the lattice. The second system is the one-dimensional semiconductor tetrathiofulvalinium bis-cis-(1,2-perfluoromethylethylene-1,2-dithiolato)copper(I), which exhibits a small, but sharp break in the magnetic susceptibility near 250°K due to a first order phase transition, and undergoes a spin-Peierls transition to a singlet ground state at 12.4°K. In order to investigate the high temperature transition, the single crystal x-ray structure was determined at 295° and 200°K. It is observed that the transition involves the freezing out of the rotation of the CF₃ groups accompanying a shift in the stacking of the molecules. The low temperature transition was investigated using calorimetry in order to measure the thermodynamic values of the transition and to compare them with the values predicted by theory.

THE MECHANISM OF NI(I)-CATALYZED OLEFIN ISOMERIZATION

Michael J. D'Aniello, Jr.

(Final Thesis)

June 15, 1976

Solutions of the Ni(I) complexes $(PPh_3)_3NiX$, $X=Cl, Br, SnCl_3$, effectively catalyze the isomerization of terminal olefins to internal olefins with an initial high selectivity for the cis isomer that appears to be anion-dependent. Since it was not obvious that these complexes effected the conversion by established mechanisms a detailed investigation was undertaken to determine the process by which these Ni(I) complexes induced isomerization. The problem was approached in three ways and the results of each are outlined below.

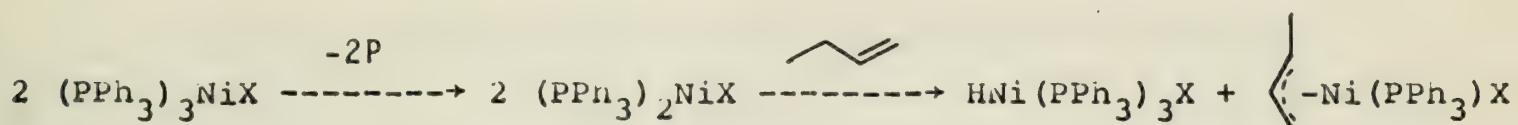
First, the kinetics of the reaction of 1-butene with $(PPh_3)_3NiSnCl_3$ were studied in both benzene and THF. Unfortunately, a rate law could not be determined due to poor reproducibility among kinetic runs. However, several kinetic trends were apparent and must be accounted for by any proposed mechanism. A nearly second order dependence was most often observed on $[(PPh_3)_3NiSnCl_3]$. A zero order dependence was found for 1-butene over the concentration range of 0.01-0.5 M. There appeared to be an inverse dependence on added PPh_3 but an order could not be determined. The rate of isomerization in benzene was greater than in THF which suggests a dependence on the donor properties of the solvent.

Another approach to the problem was to investigate the isomerization of 1-butene-3- d_2 . Intermolecular scrambling of deuterium is generally observed with catalysts based on metal hydrides while a specific 1,3-shift of deuterium occurs in systems which involve a π -allyl metal hydride intermediate. The isomerization of 1-butene-3- d_2 was carried out with $(PPh_3)_3NiSnCl_3$ in benzene and allowed to proceed to various levels of conversion. The unisomerized 1-butene-3- d_2 and its isomerization products were isolated, separated, and examined by proton NMR and mass spectroscopy. The observed intermolecular scrambling of deuterium is consistent only with a nickel hydride based mechanism. At low conversion, net transfer of deuterium from the 2-butenes to 1-butene-3- d_2 occurred which resulted in the formation of predominately mono-deuterated 2-butenes. After prolonged contact of 1-butene-3- d_2 with $(PPh_3)_3NiSnCl_3$ there was both an equal distribution of deuterium among isomers as well as a statistical distribution of deuterium within each isomer.

As a result of the labeled olefin studies which indicated that a nickel hydride was responsible for isomerization, several experiments were designed to define the nature of the hydride intermediate and the process by which it formed from the Ni(I) precursor. Treatment of $(PPh_3)_4Ni$ with HCl or $HSnCl_3$ at $-78^\circ C$ gave thermally sensitive hydrides, possibly $HNi(PPh_3)_3X$, which were very efficient isomerization catalysts and gave product ratios similar to those obtained with $(PPh_3)_3NiCl$ and $(PPh_3)_3NiSnCl_3$, respectively. These Ni(0)/acid systems were very sensitive to poisoning by 1,3-butadiene which reacted with the hydride to give a stable π -crotyl nickel complex. The Ni(I) systems were similarly affected. Addition of 0.01 mole of 1,3-butadiene per mole of $(PPh_3)_3NiSnCl_3$ stopped olefin isomerization. When the metal hydride formed from Ni(0)/acid was treated with 0.5 equivalent of 1,3-butadiene the following reaction occurred:

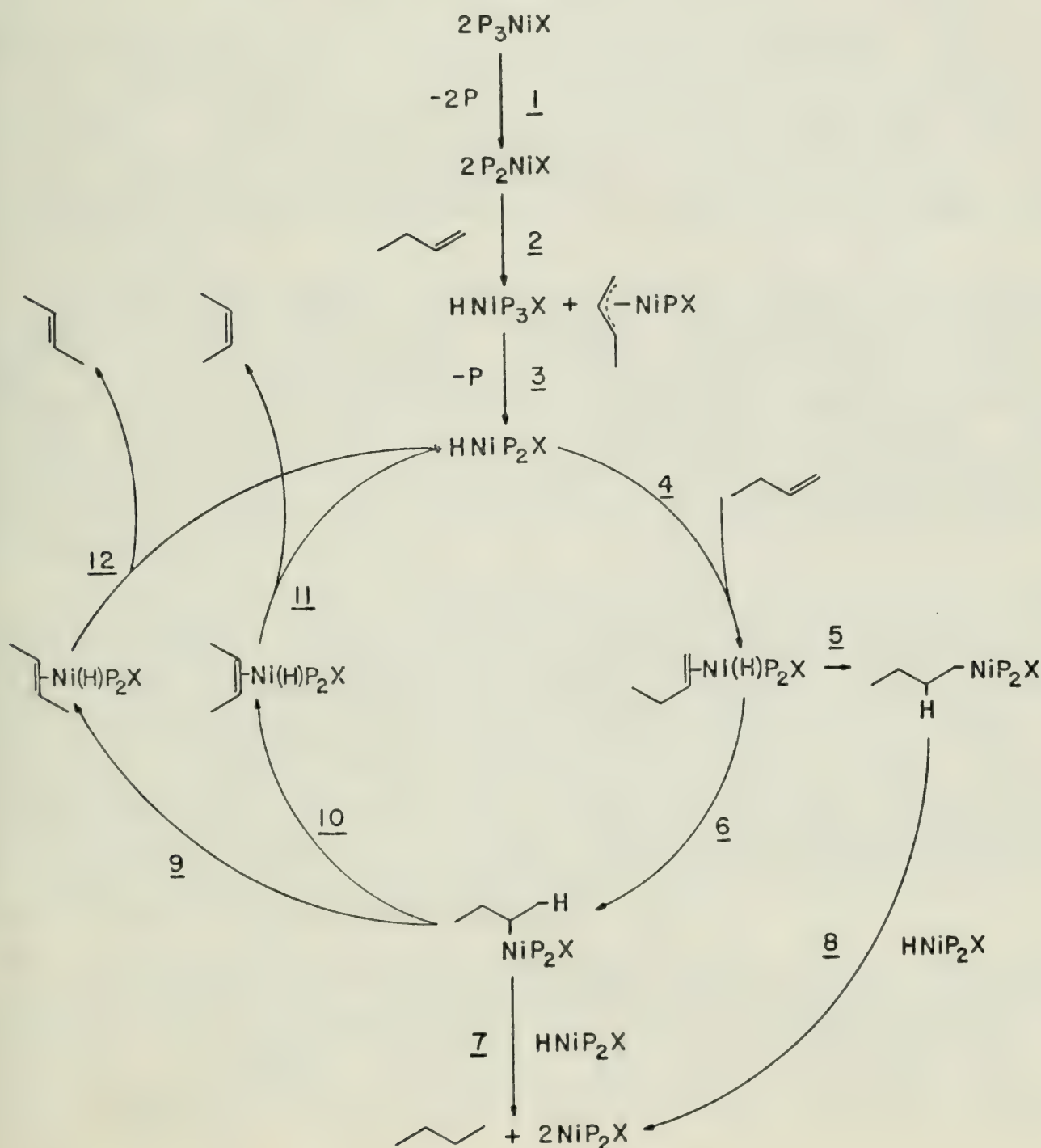


which, if reversible, would provide a source of nickel hydride in the Ni(I) isomerization systems, i.e.,



Support for this hypothesis came from the traces of π -crotyl nickel complex that were detected in Ni(I) isomerization reactions.

Formation of the nickel hydride in this fashion provides access to a standard catalytic cycle based on the metal hydride. The mechanism proposed on the basis of the above data is outlined below. The source of cis selectivity can be rationalized by a consideration of the steric requirements of the olefin metal complex intermediates.



STUDIES OF CYCLOPENTADIENYLBISLIGANDNICKEL(I) COMPLEXES

Alex N. Williamson

(Final Thesis)

June 25, 1976

A new class of cyclopentadienylbisligandnickel(I) complexes has been prepared using a variety of ligands and several preparative methods. Ligands include amines, arsines, phosphites and phosphines. Preparative methods include reductions of cyclopentadienylnickel(II) complexes, comproportionation of nickelocene and nickel(0) complexes and reactions involving oxidations of zerovalent nickel complexes.

The paramagnetic products were detected and characterized by epr spectroscopy. Predictable hyperfine splitting patterns were observed at room temperature for species containing phosphorous and arsenic donors. Hyperfine structure was not observed at room temperature for species containing nitrogen donors. Frozen solutions of the amine complexes show well resolved hyperfine structure, as do the complexes with phosphines. Additionally, rhombic spectra were observed for frozen solutions of both the amine and phosphine containing species and reflect the low symmetry of these complexes. Computer simulated spectra were obtained for amine and phosphine complexes and are in close agreement with those observed experimentally.

Complexes of suitable purity were isolated when 1,2-bis(diphenylphosphino)ethane (diphos), 1,1' bipyridyl (bipy) and di-n-butylphenylphosphine were used as ligands. Magnetic susceptibilities were determined for these complexes and are in the range of 1.69 to 1.76 B.M. Attempts to isolate others of these species were generally unsuccessful and, in some cases, Ni(0) and Ni(II) products were observed. Solutions were deep blue or violet in color, except those containing phosphites and bulky phosphines. The observation of brownish green solutions in these cases suggested that decomposition of the nickel(I) species was occurring.

To obtain information about the stability of $(C_5H_5)NiL_2$ systems, several cationic cyclopentadienylbisligandnickel(II) complexes were studied by cyclic voltammetry and controlled potential electrolysis. Although strict electrochemical reversibility was not observed for most of these systems, peak current ratios (I_p^A/I_p^C) suggest that several of the Ni(I) species generated in this manner are stable even at slow potential scan rates. Current ratios observed for the Ni(I) complex with bulky triphenylphosphine show that this species is unstable at fast scan rates. Controlled potential electrolysis of several of these systems shows that the Ni(I) complexes once generated undergo extensive decomposition. One of the electroactive decomposition products was shown to be nickelocene by the process of peak matching.

Chemical reactions of complexes with diphos and di-n-butylphenylphosphine were studied. Reactions with carbon monoxide resulted in displacement of the cyclopentadienyl ring and the formation of $(CO)_2NiL_2$ complexes. A transient $(C_5H_5)NiL_2L'$ species was detected (epr) in the reaction with $P(OCH_3)_3$ and suggests that addition of ligands and subsequent displacement of the cyclopentadienyl ring occurs in a stepwise manner.

ELECTRON EXCHANGE INTERACTIONS IN COPPER(II) AND MANGANESE(II)

OUTER-SPHERE-ASSOCIATED DIMERS; THE DYNAMICS OF ELECTRON TRANSFER

Edward J. Laskowski

(Final Thesis)

July 6, 1976

It has been observed that the rate of certain outer-sphere redox reactions involving cationic transition metal complexes is affected by anionic species in solution.^{1,2} This "anion assistance" effect gives rise to a term in the rate law for these reactions which is approximately first order in concentration of added anion and dependent on the specific anion present. For those outer-sphere redox reactions observed, it was suggested that a precursor complex was formed in which the anion is complexed with the reducing agent and participates in the electron transfer process by providing a relatively favorable "path" between the two metal ions.² If the precursor species is relatively long lived, then the rate of electron transfer between the two metals will become important in determining the overall rate of the reaction. Assuming the above interpretation to be valid, a study of the magnetic exchange interactions in a series of outer-sphere-associated metal dimers could help in further understanding the "anion assistance" effect. It was with that purpose in mind that the present study was undertaken.

A series of compounds having the formula $[\text{Cu}_2(\text{tren})_2\text{X}_2](\text{BPh}_4)_2$, where X is a halide or pseudohalide and tren is $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$, has been prepared. The compounds have been structurally and magnetically characterized. For the compounds with $\text{X} = \text{CN}^-$,³ NCO^- ,⁴ NCS^- ,⁴ and Cl^- ,⁴ the structures contain discrete BPh_4^- anions and dimeric cationic units, as shown by single-crystal X-ray diffraction studies. The two halves of the dimeric unit are connected by an outer-sphere type of bridge in which the X group is bonded to one of the copper(II) ions and also hydrogen bonded to one of the amine nitrogen atoms coordinated to the second copper(II) ion. Evidence for similar structures for the bromo- and hydroxo-bridged species is also given. It was necessary to establish that all compounds in the series contain copper ions in similar geometric environments so that complications due to differing ground states of the metal ion would not have to be considered. It has been found that by varying the X group, the magnitude of J, the electron exchange parameter in the spin Hamiltonian $\hat{H} = 2\text{JS}_1 \cdot \text{S}_2$, may change by as much as a factor of 100. Changes in outer-sphere redox rates of this order or larger have been observed for the "anion assistance" effect. The results of this study are discussed in terms of the relationship of J to the rate of electron transfer in outer-sphere redox reactions.

Additional work in developing this possible solid-state analogue of the precursor in outer-sphere redox reactions has involved changing the metal from copper(II) to manganese(II). X-ray crystallographic studies show that $[\text{Mn}_2(\text{tren})_2(\text{NCO})_2](\text{BPh}_4)_2$ and $[\text{Mn}_2(\text{tren})_2(\text{NCS})_2](\text{BPh}_4)_2$ are isostructural with $[\text{Cu}_2(\text{tren})_2(\text{NCS})_2](\text{BPh}_4)_2$. Detailed magnetic susceptibility and EPR work, including a single crystal EPR study, show these compounds to be dimeric, although antiferromagnetic exchange interactions of less than 0.20 cm^{-1} are found. The difficulties associated in obtaining precise values of J for these complexes

make further generalizations about the dynamic nature of outer-sphere electron exchange interactions impossible.

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NOVEL STUDIES OF TRANSITION METAL DIMERS

Robert M. Richman

(Final Thesis)

July 8, 1976

Part 1. Physical Studies of Rhodium Carboxylate Dimers.

The chemistry of compounds containing two or more transition metal ions has recently gained widespread attention. In an attempt to understand the acid-base and redox properties that make these systems attractive as biological and industrial catalysts, a series of physical measurements has been performed on the rhodium butyrate dimer and its one-to-one and two-to-one adducts with several Lewis bases. Isosbestic points in the electronic spectra indicate that in most cases the first mole of base binds completely before the second mole binds, and that both steps have high equilibrium constants. This facilitates the determination of the enthalpies of adduct formation of the separate steps. Using seven bases with known E_B and C_B parameters, it is not possible to obtain adequate E_A and C_A parameters for rhodium butyrate. This is explained in terms of π effects. These results motivated an electrochemical investigation of the adducts, since oxidation corresponds to the removal of an electron of π symmetry. Indeed, the measured $E_{1/2}$ values are very sensitive to the nature of the coordinated base. The spectroscopic and electrochemical results can be combined with the calorimetric results via thermodynamic cycles to estimate enthalpies of adduct formation of the rhodium butyrate ion and excited state with the bases studied. In the cyclic voltammetry experiment, it was noted that the peak potential separation differed markedly for different adducts. After correcting these data for iR drops within the cell, it has been possible to extract rate constants for electron transfer at the platinum electrode and draw some tentative conclusions about the mechanisms of electron transfer in the various adducts.

In a companion study, the similar but stronger acid rhodium trifluoroacetate has been allowed to interact with the nitroxide radical 2,2,6,6-tetramethylpiperidine-N-oxyl. The X-band and Q-band esr spectra show the presence of a one-to-one complex with rhodium hyperfine of 1.7 ± 0.2 gauss and a g shift from 2.0052 to 2.0150, the largest ever reported for a nitroxide radical. These results are interpreted semi-quantitatively in terms of rhodium's large spin-orbit coupling constant and a molecular orbital model that requires delocalization of the unpaired electron into the π^* combination of rhodium d_{xz} orbitals.

Part 2. The Rate of Thermal Intervalence Transfer in μ -pyrazine-decaamminediruthenium(5+).

The title compound has been one of the most thoroughly studied mixed valence compounds, yet there is no agreement as to even the approximate time scale at which the odd electron changes from a "localized" to a "delocalized" description. It is proposed that this rate of intervalence transfer in this and similar compounds can be determined by measuring the frequency dependence of the dipole moment in a frozen solution of the compound. Such measurements of dielectric permittivities have been done for many years by frequency domain techniques. In the

recently developed technique of time domain reflectometry, the dielectric response of the sample to a voltage pulse is Fourier transformed, yielding information over several orders of magnitude in frequency.

Preliminary results indicate a rate of $2.5 \pm 1.0 \times 10^9 \text{ sec}^{-1}$ at 250°K . The theoretical basis for estimating these rates from the Hush model is critically examined and greatly modified by a demonstration of the importance of quantum mechanical tunneling and anharmonicity in the potential energy.

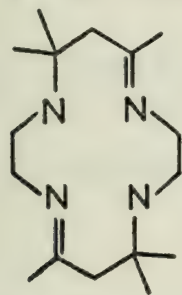
ELECTRON EXCHANGE INTERACTIONS IN DIMERIC LINEAR BRIDGED COMPLEXES OF CU(II) AND IN DIBRIDGED COMPOUNDS OF TI(III)

Rudolph G. Jungst

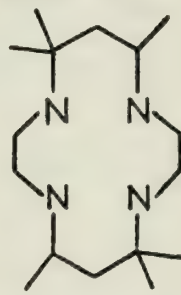
(Final Thesis)

August 24, 1976

The magnetic properties of a series of macrocyclic ligand copper complexes containing a single bridging group have been studied to determine the strength of the electron exchange interaction. A cyanide dimer of this type, $\{[\text{Cu}(\text{Me}_6(14)-4,11\text{-dieneN}_4)]_2\text{CN}\}(\text{ClO}_4)_3$, was first synthesized by Curtis.¹ The structure of the macrocyclic ligand is shown below. More recently, Bauer, Robinson, and Margerum



$\text{Me}_6(14)-4,11\text{-dieneN}_4$



tet-b

prepared and determined the X-ray crystal structure of $\{[\text{Cu}(\text{tet-b})]_2\text{Cl}\}(\text{ClO}_4)_3$ which has a single bridging chloride.² This series has now been extended by the synthesis of $\{[\text{Cu}(\text{tet-b})]_2\text{CN}\}(\text{ClO}_4)_3$ and $\{[\text{Cu}(\text{tet-b})]_2\text{N}_3\}(\text{ClO}_4)_3$. The latter is the first copper complex isolated which potentially contains a single azide bridge. Magnetic susceptibility measurements to liquid helium temperature can be simulated by an exchange term of the form $H = 2JS_1 \cdot S_2$ with J gauging the magnitude of the interaction. Results from computer fitting the data are $J = -3 \text{ cm}^{-1}$ for the cyanide dimer with the diimine ligand and $J = -144 \text{ cm}^{-1}$, -23 cm^{-1} , and -14 cm^{-1} for the chloride, cyanide, and azide dimers with tet-b. An X-ray crystallographic determination confirms that the cyanide in the diimine ligand complex is bridging and infrared spectra are consistent with end to end bridging in the CN^- and N_3^- tet-b complexes. Electronic spectra and epr studies indicate that the copper site has similar properties for the chloride and cyanide tet-b dimers, while a different distortion than has been previously investigated exists in the cyanide dimer with the diimine ligand. The difference in J for the two cyanide dimers is attributed to the change in ligand geometry about the copper atom while the tet-b chloride and cyanide compounds provide a good comparison of the effectiveness of exchange coupling through these two bridges without simultaneous effects from distortion of the nonbridging ligand geometry.

A series of trimetallic Ti(III) complexes of the form $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2\text{MX}_4$ where $\text{M} = \text{Zn}$, Be , or Mn and $\text{X} = \text{Cl}$ or Br has been prepared by Sekutowski³ and magnetic susceptibility studies indicate that the compounds with a diamagnetic central metal show antiferromagnetic coupling between the titanium atoms. The magnitude of the interaction is relatively constant when the central metal is changed from Zn to Be or the cyclopentadienyl rings replaced with $\text{CH}_3\text{C}_5\text{H}_4^-$ or $(\text{CH}_3)_2\text{Si}(\text{C}_5\text{H}_4)_2^{2-}$. Bridging bromine rather than chlorine raises the J value from about -9 cm^{-1} to -16 cm^{-1} for $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2\text{ZnX}_4 \cdot 2\text{C}_6\text{H}_6$. Coupling between the terminal titanium atoms could not be definitely proven for $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2\text{MnCl}_4(\text{THF})_2$.

Magnetic properties for $[(C_5H_5)_2TiX]_2$, $X = Cl$ or Br were also studied and substitution of $CH_3C_5H_4^-$ for $C_5H_5^-$ was found to increase the antiferromagnetic interaction for $X = Cl$. X-ray crystallographic data indicate that the increase in J parallels a decrease in metal-metal separation, implying direct overlap of metal orbitals as a possible exchange pathway. Evidence is seen in the variable temperature magnetic susceptibility data on $[(C_5H_5)_2TiCl]_2$ for impurities which are introduced during sublimation.

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THE IMPORTANCE OF SYMMETRY IN THE UNDERSTANDING OF PHASE CHANGES IN
CERTAIN THREE-DIMENSIONAL ANTIFERROMAGNETS

Jeffrey A. Kelber

November 9, 1976

A phase change can be defined as a change in the symmetry or structure of a crystal at a given temperature or pressure. Phase changes which occur in such compounds as TTF:TCNQ, $K_2Pt(CN)_4Br_{0.33}H_2O$, and various magnetic systems occur as a function of temperature only. Therefore, transitions which occur at a given critical temperature are of current interest to chemists.

Phase changes can generally be classified as first or second order, depending on whether or not the transition between phases is discontinuous or continuous.¹ The mean field theory developed by Landau² fails to correctly predict the first-order transition in several three-dimensional antiferromagnets.³ Mukamel, Krinsky, and Bak,³⁻⁵ using renormalization group methods, have developed a new criterion for predicting the order of the phase transition in certain compounds. This theory, based upon symmetry considerations rather than upon detailed physical interactions within the lattice, corrects the discrepancies of the Landau theory and predicts that the transitions of several other compounds are first order.³ Bak also predicts that impurities in these compounds will lead to a gradual rounding or smearing of the discontinuity of the first order transition.⁶

Recently experimental work has been done on two of the compounds predicted to undergo first order transitions: $TbSb^7$ and $ErSb.^{8-10}$ While the results are not conclusive, the weight of the evidence currently supports the new theory.

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HETEROGENEOUS CATALYSIS BY ZEOLITES

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Introduction

In 1960, Weisz and Frilette¹ disclosed the first application of zeolites to catalysis by selectively cracking n-paraffins with NaX and CaX zeolite. This discovery spurred an intensive research and development effort which has led to the commercial use of metal-substituted zeolites to crack over four million barrels of petroleum per day.² This research has shown that the catalytic and physical properties of zeolites can be extensively modified, allowing chemists to "engineer" a highly selective catalyst for an extremely broad range of reactions.³

Zeolite Composition

Zeolites are crystalline aluminosilicate compounds which form porous, three-dimensional frameworks of TO_4 ($T=Si, Al$) tetrahedra which are linked through the oxygen atoms to form polyhedra which interconnect to form channels and cages. Charge balance is provided by cations located in several different environments within the framework. In general, the cations can be exchanged by other cations as long as steric and electronic requirements are fulfilled. Some 34 naturally-occurring zeolites have been identified while over 90 synthetic zeolites have been characterized. The most common zeolites which are used as catalysts are the synthetic faujasites NaX and NaY which have a range of stoichiometries $Na_{77-96}(AlO_2)_{77-96}(SiO_2)_{120-100} \cdot nH_2O$ and $Na_{49-76}(AlO_2)_{49-76}(SiO_2)_{143-121} \cdot nH_2O$, respectively, having pore openings of 8-10 Å.^{3,4} The sodium ions can be exchanged for a great variety of cations, including transition metals, lanthanides, and organic cations. NaX and NaY are synthesized from aqueous gels of $NaAlO_2$, sodium silicate, NaOH, and colloidal SiO_2 at about 100 °C. The products obtained are dependent on the concentration of water, the Si/Al ratio, the temperature, pressure, and reaction time.⁵

Catalytic Facility

A great deal of research has been directed toward discovering the variables which control the catalytic properties of zeolites.³ Some of these are the zeolite pore size and shape, the cations present and their oxidation state, the state of hydration, the Si/Al ratio, impurities in the framework (e.g., Fe^{3+} , Ga^{3+} , Ge^{4+}), and the temperature treatment of the zeolite. An example of this is demonstrated by NaX, which has no activity in the hydrogenation of olefins, and by NiX, which readily hydrogenates olefins, including phenol to give cyclohexanol.⁶

A wide variety of organic reactions can be catalyzed with high selectivity by employing the properly modified zeolite. Because of their size and shape selectivity, high activity, broad range of reactions, and ease of modification, zeolites have been compared to enzymes. However, zeolites have the advantage of being stable over a broad range of reaction conditions.³

Physical Measurements

The nature of the active sites in zeolites has been investigated by many techniques including ir, nmr, and epr spectroscopy.⁷ Unfortunately, much of this work is of little value because of the lack of adequate purification and characterization of materials.^{8,9} Most workers have relied on x-ray powder diffraction and elemental analysis for characterization, but these techniques may not be sensitive enough to detect all the important variables such as trace metal impurities and the distribution of cations in the various sites in the zeolite.

A technique for growing large single crystals of zeolites has recently been developed by Seff and coworkers¹⁰ and they have reported the first high-resolution single-crystal x-ray results of adsorbed molecules in substituted zeolite A. When the zeolite is dehydrated, the metal ions become highly coordinatively unsaturated and can bind ligands such as acetylene, CO, and NO to give structures which appear similar to complexes well known in organometallic chemistry: C₂H₂ binds side on with M-C=2.6 Å; CO binds linearly with M-C=2.3 Å; NO gives a bent complex with M-N-O bond angle of 140° and M-N=2.4 Å and N-O=1.5 Å. No results have been reported on the catalytically more interesting zeolites X and Y.

In a recent x-ray photoelectron study of nickel substituted NaY zeolites, Minachev, et. al.,¹¹ observed that upon reaction with CO at 400 °C, Ni(O) and an intermediate form of Ni which they referred to as Ni⁺ were obtained. They attributed the stabilization of Ni⁺ to the formation of Ni complexes with adsorbed CO.

Catalysis Mechanism

A number of workers have postulated that small metal clusters form in the supercages of transition metal substituted zeolites upon reduction by hydrogen at high temperatures.^{12,13,14} Beyer, Jacobs, and Uytterhoeven¹⁴ recently studied the kinetics of hydrogen reduction of AgY zeolite using ir spectroscopy and x-ray spectrometry. They concluded that the silver ions migrate out of the smaller cages into the supercages to form Ag₃⁺ clusters, while at very high temperatures, Ag crystallites formed on the outside of the zeolite framework and were observable by electron microscopy. The evidence for the formation of metal clusters is not yet conclusive, but some interesting analogies from homogeneous catalysis by metal cluster compounds may exist if that evidence is forthcoming.

Conclusion

In conclusion, zeolites are useful and interesting compounds which are very active heterogeneous catalysts. Since these are crystalline materials, chemists may be able to gain insight into the mechanisms of heterogeneous catalysis through the study of the intimate details of the structures, reactions, and physical properties of these materials.

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MÖSSBAUER SPECTROSCOPY APPLIED TO SUPPORTED METAL CATALYSIS

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INTRODUCTION

Reactions catalyzed by transition metals and metal compounds are industrially important. The details of the catalyzed reactions are generally not understood completely. Recently, several physical techniques have been used to investigate catalytic reactions which occur on surfaces. The kinetics and mechanisms of the reactions and the nature of the surface before, during, and after the reaction are being studied.

Several investigations of catalytic reactions have concerned metals supported on inert carriers, such as aluminum oxide, silica, magnesium oxide, and graphite to mention a few. Supported metal catalysts have the advantages of possessing high surface area, maintaining small particles on the support, and requiring a small quantity of metal to prepare the catalyst.

Since 1963, Mössbauer spectroscopy has experienced increasing use in the study of supported catalysts. The Mössbauer effect, a recoil free emission and absorption of gamma rays, was discovered in 1957 by R. L. Mössbauer during his graduate work. This effect is exhibited by 44 nuclei, of which ^{57}Fe and ^{119}Sn have been most widely studied. The parameters obtained in the Mössbauer experiment can be useful to characterize the electronic state and the symmetry about the metal in the supported catalyst, as well as the oxidation-reduction behavior and particle size distribution, which cannot be determined easily by conventional techniques.¹

IRON OXIDE

Mössbauer parameters have proved useful in characterizing supported iron oxide catalysts. The strength of interaction of iron with various supports has been correlated to the ease of reduction of the ferric species on the supports as monitored by Mössbauer spectroscopy.² This type of information is important in understanding the catalytic properties of iron oxide on various supports and may aid in catalytic design. Mössbauer spectroscopy has been used to study chemisorption onto supported iron oxide and the penetration of particles into iron oxide to give insight into intermediates found in catalytic reactions such as dehydrogenation or isomerization.³

BIMETALLIC SYSTEMS

Bimetallic catalysts have evoked interest in catalysis studies because the reactivity and selectivity of the bimetallic species differs from the individual components. In the majority of studies, the bimetallic catalysts have been in the form of powders, wires, and films. Recently, supported bimetallic catalysts have been investigated. To

date, there are two Mössbauer studies considering supported iron alloyed with Pd or Pt.^{4,5} Mössbauer spectroscopy has enabled the workers to characterize the iron species on the support as to the chemical state, symmetry, and concentration of surface iron. Reversible oxidation-reduction behavior is observed and this supports the fact that the iron is associated with either the Pd or Pt as clusters on the support.

ZEOLITES

Another example of supported metal catalysts which has been widely used in industry is that of transition metals exchanged into zeolite lattices. It is found that the catalytic activity and selectivity is specific to the particular lattice with its characteristic geometry and pore size. Mössbauer spectroscopy has served to locate the nucleus in the various channels, cages, and pockets of the zeolite by monitoring the adsorption behavior, oxidation-reduction behavior and by comparison of parameters with compounds of known coordination number and chemical state.⁶ Workers have used information derived from Mössbauer experiments to rationalize the catalytic activity and selectivity of various iron zeolites.

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HIGH POTENTIAL IRON SULFUR PROTEIN AND THE THREE STATE HYPOTHESIS

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Introduction

The high potential iron sulfur protein (HP) of the purple sulfur photo-synthetic bacterium, Chromatium vinosum, is an electron transfer protein¹ containing four iron and four inorganic sulfur atoms. The cluster arrangement of the iron and sulfur atoms² is identical, within experimental error, to that found in the two iron-sulfur clusters of the eight-iron-eight-sulfur ferredoxin (FD) of Peptococcus aerogenes. However, the properties of the two protein types differ considerably. The redox potentials of HP and both 8-Fe-8-S and 4-Fe-4S ferredoxins differ by over 700 mV.³ It is reduced FD which exhibits an epr spectrum, whereas it is the oxidized form of HP which exhibits an epr spectrum.³ These observations have led to the proposal that the cluster exists in three oxidation states.^{2,3}

C ⁻	C	C ⁺
FD(red)	FD(ox)	[FD(s-ox)]
[HP(s-red)]	HP(red)	HP(ox)

Physical Studies

Several physical techniques have been employed to examine the properties of HP and FD of Clostridium pasteurianum. Information about the magnetic properties has been obtained for both proteins by proton magnetic resonance studies in the temperature range 5 to 40° C^{4,5,6,7} and, for HP, by direct susceptibility measurements at low temperatures.^{8,9} The pmr contact shift studies indicate that the iron sites in FD(red) follow the Curie law, that both HP(red) and FD(ox) behave in a non-Curie fashion, and that two types of iron sites are present in HP(ox). Magnetic susceptibility data are consistent with the proposed antiferromagnetic nature of the HP cluster at low temperatures. Electron paramagnetic resonance studies have revealed only a single axial-type signal for FD(red)^{11,12}, whereas K-band studies of HP(ox) have revealed the presence of two equally populated sites of rhombic and axial symmetry.⁹ The signal of HP(s-red)¹³ is very similar to that of FD(red). Mossbauer studies¹⁴⁻¹⁷ lend further support to the three-state hypothesis. The spectra of FD(ox)¹⁶ and HP(red)¹⁷ show similar isomer shifts and Zeeman behavior. The Mossbauer spectra of HP(ox),^{15,17} in agreement with the epr spectra, show the presence of two different types of iron sites. The FD(red)¹⁶ and HP(s-red)¹⁴ spectra have similar isomer shifts but otherwise differ.

Structure of the Proteins

Structural determinations for HP and FD have revealed some fundamental differences in the proteins which may account for the extremely different characteristic properties.¹⁸⁻²² The relative positions in the proteins of the cysteines^{18,19} which bind the Fe₄S₄ clusters differ considerably, and this is reflected in the position of the cluster relative to the intramolecular interface.¹⁸ A comparison of the oxidized and reduced forms of HP has revealed

changes in the cluster structure ¹⁸ which provides an explanation of the observed epr, pmr, and Mossbauer spectra. The possible role of tyrosine in the electron transfer process has been examined. ¹⁸

Conclusion

The results of the studies conducted to date appear to support the three state hypothesis first proposed by Carter ^{23,24} in 1972. The hypothesis has provided a viable explanation of the extremely different properties of the two protein types

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STRUCTURE OF CYCLOPHOSPHAZENES IN RELATION TO THEIR METAL COMPLEXES

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INTRODUCTION

Cyclophosphazenes are of the general formula $(NPR_2)_n$ where -R can be a wide variety of groups including halogens, amines, alkoxides, alkyls, and aryls.¹ Compounds have been characterized having ring sizes from 6 through 18 atoms. It is the reaction of ammonium chloride and phosphorus pentachloride which provides the most convenient route for synthesis of chlorophosphazenes, $(NPCl_2)_3$,^{2,4,5} They are themselves used as precursors in substitution reactions to replace the chlorines by other types of groups.³ Phosphazenes have been used as inorganic polymers,⁴ as clathrates⁵ in the separation of organic compounds, as fertilizers,⁶ and as flame retardant materials for textiles.

BONDING IN CYCLOPHOSPHAZENES

The phosphazene ring is known to be significantly more stable than can be accounted for by N-P single bonds. At the same time one must account for equal P-N bond lengths and a low barrier to rotation around the P-N bond. Four models each with its own support have been used to explain these facts. The simplest model consists of ionic interactions whereby the nitrogen atoms are assigned a partial negative charge and the phosphorus atoms a partial positive charge. Some recent ESR work supports this model⁷. In the second model Paddock postulates a "benzene-like" delocalization where π -bonding between nitrogen p_z and phosphorus d_{xz} orbitals is suggested by increasing ionization potentials⁸ and P-N bond energies as ring size is increased. The third is Dewar's three center island model for $p\pi-d\pi$ bonding⁹ which is supported by uv spectral data and Faraday effect measurements.¹⁰ The fourth model accounts for stabilization through P-P transannular bonding, and this possibly is suggested by CNDO/2 molecular orbital calculations.¹¹

COMPLEXES OF PHOSPHAZENES

Metal complexes of phosphazenes were found to form most easily with aminophosphazenes¹² where coordination is at a ring nitrogen atom. This is consistent with basicity studies of the ring nitrogen atoms.¹ Protonation of aminotricyclophosphazenes has a pronounced effect on the ring bonding. An alternation of bond lengths is induced indicating the breaking of the ring conjugation.^{13,14} These effects are also observed in the tetramers^{15,16} as well as a pronounced closing of the N-P-N ring bond angles due perhaps to the additional electron withdrawal from the ring.

The molecule $N_6P_6(NMe_2)_{12}$ has been used as a macrocyclic ligand to form a number of complexes.¹⁷ Structural studies have been done on a $Cu(II)$ ¹⁸ and a $Co(II)$ ¹⁹ complex with a chloride ion occupying a fifth and equatorial coordination site. The macrocycle folds to block the possibility of a sixth ligand coordinating. These compounds provide the opportunity to observe both ring conformation and axial and equatorial coordination.

With $N_4P_4(NMe_2)_8W(CO)_4$ ²⁰ we have an example of coordination both to the ring and to the exocyclic amine as opposed to coordination by two ring nitrogen atoms as in $N_4P_4(NHMe)_8PtCl_2$.²¹ The tungsten complex allows an examination of exocyclic coordination and gives an example in which the phosphazene is not symmetrically bound.

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cis-DIAMMINEDICHLOROPLATINUM(II) AND ITS ANALOGS:

THE SEARCH FOR A CURE FOR CANCER

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Introduction

While the discovery that cis-Pt(NH₃)₂Cl₂ had activity in biological systems was accidental, the discovery of its anti-tumor properties was the result of systematic study.¹ A major aim of present research efforts is to develop better anti-cancer drugs analogous to this compound. If this is to be accomplished in other than a random fashion, inquiries must be made into the mode of action of these compounds on cancer tissue.

Biological Effects

Early studies showed that cis-Pt(NH₃)₂Cl₂ does not concentrate in tumors,² but it was recognized that the complex had an effect on cell division. Recent studies on tumor cells show that cell division is blocked in metaphase, but protein and RNA synthesis remain active.³ Aggarwal⁴ notes a clear band around the nucleus, indicating the absence of microfilaments (probably due to their depolymerization). Although disruption of cell division has been proposed as the mechanism for the anti-tumor action of the complex, Rosenberg⁵ has proposed that cis-Pt(NH₃)₂Cl₂ and its analogs activate an immune response against cancer cells. He cites, among other things, the correlation between the ability of a complex to induce lysis in lysogenic bacteria and its ability to inhibit tumor growth. It should be noted that cis-Pt(NH₃)₂Cl₂ has been shown to repress the immune response in certain instances.⁶ It is not yet clear which of the two mechanisms is more important in curing cancer.

The Chemistry of cis-Pt(NH₃)₂Cl₂

The complex cis-Pt(NH₃)₂Cl₂ is fairly reactive, undergoing displacement of the chloride ligands by a variety of nucleophiles (e.g., $k_{\text{aquation}} = 2.5 \times 10^5 \text{ sec}^{-1}$).⁷ However, the dichloro form is most likely the active form present in the cell.⁸ cis-Pt(NH₃)₂Cl₂ is known to react with amino acids and proteins, but these reactions do not seem to be of much importance in the anti-tumor activity of the complex.^{9,10} Interactions with DNA have been studied extensively. Interstrand¹¹ and intrastrand^{12,13} have been proposed to explain the activity of the complex, although certain evidence suggests that interstrand crosslinks are unimportant.^{12,14} The site of platinum binding is most probably the guanosine N(7)^{15,16} and the platinum seems to be bound in a bidentate manner.¹⁷

Relating Structure to Activity

Since the discovery of the anti-tumor activity of cis-Pt(NH₃)₂Cl₂ was empirical, if not accidental, we have no reason to believe that it is the best drug in its class. Efforts to design better drugs should be aided by "Rosenberg's Rules."⁵ Several structure-activity relationship studies have been undertaken,^{18,19} but no conclusive results have been reported.

Conclusion

Through the efforts of researchers in this field, more effective compounds have been found (e.g., the "platinum-pyrimidine blue" complexes).⁵ Further efforts will lead, one hopes, not only to yet more effective complexes, but to an understanding of the mode of action of these platinum species and even to a better understanding of the nature of cancer.

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STUDIES OF SOME DYNAMIC METAL CARBONYL CLUSTER COMPLEXES

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December 7, 1976

Interest in the study of relatively small, discrete polynuclear compounds containing metal-metal bonds, or clusters, is steadily increasing. This is in part due to the use of clusters as models for the structures and mobility of chemisorbed species on metal surfaces and for the elucidation of reaction mechanisms in heterogeneous catalysis. The dynamic behavior of three classes of ligands, namely hydrides, carbonyls, and hydrocarbon species, in a cluster has been examined in detail through the use of NMR.

In an attempt to distinguish between the proposed mechanisms for hydride scrambling, edge-terminal-edge and edge-face-edge, the hydrido cluster $\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{Diphos})$ [Diphos = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$] was synthesized. The slow exchange ^1H NMR spectrum indicates that only one isomer is present with four nonequivalent hydride sites. Of the two structures consistent with the observed P-H splittings, one structure with a chelating diphos and the other with a bridging diphos, the latter is assumed to be correct. At room temperature, 3 of the 4 sites have been equilibrated. Computer simulated spectra based on all the possible permutations for averaging the three sites were generated. Only simulations of three of these permutations closely resemble the experimental spectra. They uniquely correspond to a physical process consisting of an edge-face-edge hydride scrambling scheme.

Through the use of ^{13}C NMR, information concerning carbonyl and hydrocarbon ligand mobilities in a series of triosmium clusters of the formula $\text{Os}_3(\text{CO})_{10}(\text{diene})$ has been obtained. The limiting low temperature spectra are consistent with the diene unit coordinated to one Os atom either in an unsymmetrical axial-equatorial or a symmetrical "bicapped" fashion. Although the diene ligand is not transferred from one Os to another, the NMR line shape behavior for conjugated dienes suggests that the initial site exchange process involves concerted restricted or complete pseudo-four fold rotation of the diene and two adjoining carbonyls. At higher temperatures, intracluster CO scrambling occurs, presumably through a tribridging intermediate, where 3 CO's are bridging the edges of the Os_3 triangle. In the case of nonconjugated dienes, such as norbornadiene, the initial rearrangement process involves a tribridging intermediate, with a combination of mechanisms proceeding at higher temperatures.

Additional studies are being conducted to determine the generality of the above mechanisms for ligand mobility in clusters.

General References

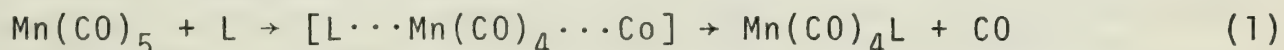
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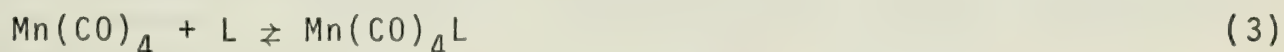
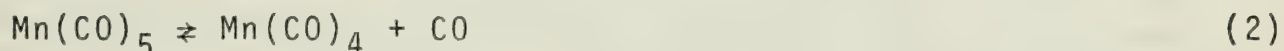
December 9, 1976

Since 1969, several mechanistic studies have been carried out on the Lewis base substitution of $\text{Mn}_2(\text{CO})_{10}$. Several mechanisms for the substitution have been proposed. It is now generally agreed that the first step is rupture of the Mn-Mn bond to form the 17 electron $\text{Mn}(\text{CO})_5$. The substitution of $\text{Mn}(\text{CO})_5$ before it recombines to yield substituted dimer is not well understood. Therefore the photochemical reactions of $\text{Mn}_2(\text{CO})_{10}$ with PBU_3 or $\text{P}(\text{OEt})_3$ have been studied. The $\text{Mn}(\text{CO})_5$ radical was generated by irradiation of the absorption at 350 nm, corresponding to the $\sigma \rightarrow \sigma^*$ transition in $\text{Mn}_2(\text{CO})_{10}$. The intensity of the light source was determined by $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$ actinometry.

There are two likely mechanisms for the substitution of $\text{Mn}(\text{CO})_5$; a 2nd order path involving a 19 electron intermediate, (1)



and a dissociative mechanism involving a 15 electron intermediate (2-3).



The distribution of substituted dimers is different for PBU_3 and $\text{P}(\text{OEt})_3$. PBU_3 forms $\text{Mn}_2(\text{CO})_8\text{L}_2$ and $\text{Mn}(\text{CO})_3\text{L}_2$, while $\text{P}(\text{OEt})_3$ forms $\text{Mn}_2(\text{CO})_8\text{L}_2$, $\text{Mn}_2(\text{CO})_7\text{L}_3$, and $\text{Mn}(\text{CO})_3\text{L}_2$. This difference is probably due to a difference in steric requirements of the ligands. However, the quantum yield and the pseudo first order rate constant for disappearance of $\text{Mn}_2(\text{CO})_{10}$ are the same in both cases and are independent of the concentration of L. Saturating the solution with CO lowers both the quantum yield and the rate constant.

The data are in best agreement with the dissociative mechanism. The results may be generalized to provide a working hypothesis: When a single electron occupies a stereochemical site in a metal carbonyl radical it induces lability.

HIGH PRESSURE EFFECTS ON TRANSITION METAL COMPLEXES

Virgil L. Payne

February 8, 1977

Introduction

In much of scientific research, observation of the change in a property of a system with temperature is a common means of studying the system. Within the past twenty years, a substantial effort has been made in the development, refinement and application of high pressure (>1 kbar = 987 atmospheres) techniques to the study of physical and chemical behavior. These techniques have been responsible for the synthesis of new materials, the study of kinetics and mechanisms of reactions and the structural and electronic characterization of compounds.^{1,2}

Experimental Apparatus

Much of the development of experimental high pressure apparatus^{3,4} is due to the pioneering work of P. W. Bridgeman in the 1940's and 50's. Utilizing what he termed the "principle of massive support," Bridgeman constructed a simple anvil device for electrical resistance measurements which would generate pressures to 50 kbars. Drickamer has modified the Bridgeman device by tapering the anvils to create a radially decreasing pressure gradient. When using NaCl as the pressure-transmitting substance, this cell can be used with optical techniques to pressures of 200 kbars. Another modification of the Bridgeman device used with optical techniques is that of the Diamond Anvil Cell (DAC).⁵ The anvils are Type II diamonds which absorb radiation at ~ 2000 cm^{-1} , but are transparent below 1000 cm^{-1} and can generate pressures in excess of 350 kbars. Various modifications of these and other devices have been made for low and high temperature work.

Calibration of high pressure devices has been based on distinct changes in electrical resistance of such materials as Iron, Barium or Bismuth.^{3,6} In recent years, the optical devices have been calibrated using methods based on the pressure-dependent changes in the fluorescence spectrum of such materials as ruby.⁷

Applications

Ferraro and coworkers^{8,9} have examined several transition metal complexes in order to observe structural nonrigidity in the solid state. They have observed conversion of tetrahedral $\text{Ni}(\text{BzPh}_2\text{P})_2\text{Br}_2$ to its square planar isomer and also trigonal-bipyramidal $\text{Ni}(\text{CN})_5^{3-}$ to its square-pyramidal isomer. In both cases, the complexes exist as a mixture of isomers at ambient pressure with conversion to only one isomer occurring upon application of sufficient pressure.

Six-coordinate complexes have not been found to undergo structural changes, but a few undergo interesting electronic changes. Drickamer and coworkers¹⁰ have observed both high spin to low spin and low spin to high spin state changes in bis- and tris(phenanthroline) iron(II) complexes as well as reduction of Fe(III) to Fe(II) in β -diketone complexes. These findings are interpreted as increased covalency in the metal-ligand bond, decreased π -backbonding and variation of electronic properties of the ligand with pressure.

Poorly conducting one-dimensional complexes such as metal glyoximes¹¹ and $\text{MPt}(\text{CN})_4$ ($\text{M}=\text{Ba}^{+2}, \text{Sr}^{+2}, \text{Mg}^{+2}$)¹² experience a dramatic increase in conductivity with pressure, although metallic behavior cannot be achieved using nondestructive methods. Similar behavior has also been observed in mixed-valence complexes of Platinum and Palladium.^{13,14} Variation of temperature and pressure has revealed evidence for a sharp metal-to-semiconductor transition in $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.30}(\text{H}_2\text{O})_3$ (KCP).¹⁵ This is interpreted in terms of increased interchain coupling which would suppress the Peierl's distortion. Superconductivity of KCP under pressures > 70 kbars is a possible consequence of this behavior.

Conclusion

The further development of high pressure techniques capable of extending the range of pressure should continue to provide chemists and physicists with a better understanding of the structure, physical properties and behavior of materials.

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RADICAL CHAIN PATHWAYS IN SUBSTITUTION REACTIONS OF METAL CARBONYL COMPOUNDS

Ma'mum Absi-Halabi

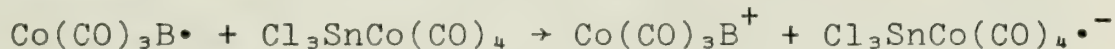
(Final Seminar)

March 1, 1977

Metal carbonyl compounds have long been known to undergo substitution by either dissociative, associative, dissociative interchange or ligand migration mechanisms. However, recent work on some carbonyl metal hydrides and manganese carbonyl compounds has revealed evidence of novel substitution pathways¹ proceeding by carbonyl radical intermediates.

The reactions of $\text{Cl}_3\text{SnCo(CO)}_4$ with some group V bases, resulting in the formation of the ionic compounds, $[\text{Co(CO)}_3\text{B}_2][\text{SnCl}_3]$, have been investigated under various conditions. It has been observed that oxygen, galvinoxyl, tetracyanoethylene and trichlorobromomethane inhibit the reactions. On the other hand, visible radiation from a fluorescent lamp or one electron donor compounds such as anhydrous Cr(acac)_2 promote the reactions. The order of the reaction with respect to the metal carbonyl is $3/2$, and the estimated ratios of the observed rate constants for AsPh_3 , PPh_3 and PBu_3 are approximately 1:150:16000.

These results suggest that the reactions proceed by a free-radical chain mechanism. The chain is initiated by homolytic cleavage of the metal-metal bond, resulting in formation of a $\text{Co(CO)}_4\cdot$ radical which undergoes rapid substitution with the base. An important step in the mechanism is an outer-sphere electron transfer process from a $\text{Co(CO)}_3\text{B}\cdot$ radical to a $\text{Cl}_3\text{SnCo(CO)}_4$ molecule:



Although our observations are new to the field of mechanistic studies of metal carbonyls, similar ones have been reported² in organic chemistry. Furthermore, numerous substitution reactions of metal carbonyls, such as V(CO)_6 , $\text{Co}_2(\text{CO})_8$ and $\text{Mn}_2(\text{CO})_{10}$, apparently proceed by pathways analogous to the one we have proposed. This is verified by results obtained for the dicobalt octacarbonyl reactions with PPh_3 and PBu_3 .

Our results add further evidence for the importance of carbonyl radicals in substitution reactions of metal carbonyls. Moreover, a new phenomenon in metal carbonyl mechanistic studies has been established, namely, electron transfer processes promoted by base substitution.

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ELECTROCHEMICAL METHODS IN BIOINORGANIC CHEMISTRY

Steven L. Suib

March 24, 1977

Introduction

The science of electrochemistry during the last 20 years has gone through a period of great growth and change.¹⁻⁷ Recently a substantial effort has been made to develop electrochemical techniques that are particularly applicable to the fields of bioelectrochemistry and bioenergetics. Several model systems have been studied to obtain information concerning analytical measures of concentration and the kinetics and mechanisms of bioinorganic reactions.

Techniques

Pulse polarographic techniques have been developed mainly to obtain increased sensitivity and resolution for analytical measurements of concentration.^{8,9} The improvements manifested in differential pulse polarography (DPP) are about three orders of magnitude better than those of d.c. polarography. In addition, information concerning specific oxidation states and complexation can be obtained, however, pulse techniques are rarely used for diagnosis of electrode processes.

Cyclic voltammetry has been widely used to investigate the reversibility of electron transfer reactions.^{10,11} It is now a powerful technique for studying irreversible electron transfer processes, electron transfer reactions preceded or followed by relatively slow chemical reactions, and adsorption effects at electrodes. In addition, the results of theoretical calculations have made it possible to use cyclic voltammetry to measure standard rate constants.

Kuwana, Heineman and Winograd have been the main workers in spectroelectrochemistry, which entails the use of an optically transparent electrode (OTE).¹²⁻¹⁴ The main utility of the OTE is in elucidating electrode reactions and determining stoichiometry, energetics, molar absorptivities and diffusion coefficients of electrogenerated intermediates or products.

Applications

Holm has recently studied iron-sulfur proteins using d.c. polarography, cyclic voltammetry and differential pulse polarography.^{15,16} Using differential pulse polarography, a mixture of the 2Fe-2S* dimer $(\text{Fe}_2\text{S}_2(\text{SPh})_4)^{-2}$ and the 4Fe-4S* cluster $(\text{Fe}_4\text{S}_4(\text{SPh})_4)^{-2}$ has been electrochemically assayed.¹⁶

Correlations of kinetics and experimental parameters have made it possible to diagnose criteria so that unknown systems can be characterized. The variations of peak current, half-peak potential or ratio of anodic to cathodic peak currents are studied as a function of rate of voltage scan.¹⁰ Typical bioinorganic systems exploiting these diagnostic criteria are

featured in the work of Bard¹⁷, Holm¹⁵, and Pickett.¹⁸ Jordan and coworkers¹⁹ have determined rate constants for various cytochrome c models using the method described by Nicholson and Shain.¹¹

Spectrocoulometry with an optically transparent electrode cell has provided information about the bioelectrochemistry of cytochrome c and cytochrome c oxidase.¹² Since heterogeneous electron transfer from these hemes to the electrode is slow, redox titrations have been performed by the coulometric generation of mediator titrants. The specific mechanisms of the electrode reactions and the rate constants for this system have been analyzed.

Summary

Differential pulse polarography, cyclic voltammetry and spectroelectrochemistry are only a few of the techniques that can provide simple, rapid and reliable results for the bioinorganic chemist. The main offerings of electrochemistry will undoubtedly be in the realm of electrode mechanisms and associated kinetics. In time, more chemists, biologists, physiologists and clinicians will work hand-in-hand with the electrochemist to understand systems which cannot be unraveled by the usual chemical methods.

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ELECTRON TRANSPORT IN CHLOROPHYLL

John R. Long

March 29, 1977

The role(s) of the numerous types of chlorophylls in photosynthesis are of contemporary research interest. It has been found that photosynthetic plants and bacteria consist mainly of antenna chlorophyll molecules:^{1,2,3} they, along with carotenoids, serve to collect the light energy and funnel it to a "complex" that converts it to a useful form of chemical energy. Such a complex is referred to as the "reaction center," symbolized as P_{λ} (λ designates the principle absorption of the complex, 700 nm in plants, and 870 nm in bacteria).^{4,5}

CHLOROPHYLL DIMER

As a result of this absorption of energy by the reaction center, there are several changes in the near IR region of the absorption spectra. The bands that change are believed to originate from bacterio chlorophyll molecules (BChl, indicating that the chlorophyll originated from bacteria); this implicates BChl with the reaction center. Similar changes occur upon mild chemical oxidation of the samples, implying that normal photosynthesis involves oxidation of a BChl complex.^{4,5,6,7} Irradiation of in vivo samples with red light yields an ESR active species having a line width equal to $1/\sqrt{2}$ that of in vitro monomeric BChl.² ENDOR studies have shown that the hyperfine coupling constant of the in vivo BChl is 1/2 that of in vitro BChl.¹⁵ These results are best interpreted in terms of a dimeric BChl complex. If the reaction center is held at a low redox potential, -100 mv, triplet ESR spectra exhibiting ESP and reduced zero field splitting parameters (relative to in vitro monomeric BChl) are observed. These observations are best interpreted in terms of delocalization of the electrons over more than one BChl molecule.⁸⁻¹⁴ The optical spectra are also consistent with a dimeric structure.^{1,2,11}

REACTION MECHANISM

The primary photochemical reaction is considered to be the transfer of an electron from an excited "BChl special pair," P^* , to some primary electron acceptor, X, such that P^+ and X^- are formed.⁴⁻⁶ If the redox potential is made low enough, ~ -100 mv, such that X is prereduced, the optical spectra show the presence of a short ($\tau < 10$ ns) and a long lived ($\tau = 6$ μ s) state, labeled P^F and P^R respectively.^{5,6,16,9,17} Analysis of the kinetics, down to the picosecond time scale, of these states reveals that P^F forms directly from P^* and that the state P^F itself involves some form of charge or electron transfer.^{6,9} Other optical studies have shown that P^F also forms as an intermediate in the normal (ie., X is not prereduced) primary photochemical process.¹⁶ These two pieces of information indicate that there must be an intermediate electron acceptor, symbolized I. ESR and optical data indicate that this species is most likely a bacteriopheophytin (BPh).^{9,19} At the present, P^F is the only observable intermediate in the normal photo-oxidation of P.

The other transient state, P^R , forms directly from P^F and only forms under conditions where X is prereduced.⁵ P^R is believed to be the ESR observed triplet. The nature of P^F is quite controversial, speculations range from charge transfer within the BChl reaction center: $[BChl^+ \cdots BChl^-]$, to simply an oxidized BChl dimer: $[BChl^+ \cdots BChl]$.^{5,8,9,10,18,19} Steady state ESR studies of reaction centers have shown a signal which is attributed to the primary electron acceptor, X, which appears to be a ubiquinone molecule (UBQ). Pico-second studies have also shown that UBQ acts as the primary electron acceptor.^{20,21}

A large volume of experimental data has been amassed, yet the same data is still subject to numerous interpretations. Present and future work lies in unambiguously identifying the exact character of the different species/states that are formed.²²

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STRUCTURAL AND ELECTRONIC PROPERTIES OF BIS(CYCLOPENTADIENYL) TITANIUM AND VANADIUM COMPOUNDS

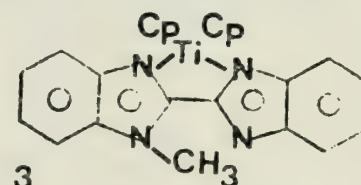
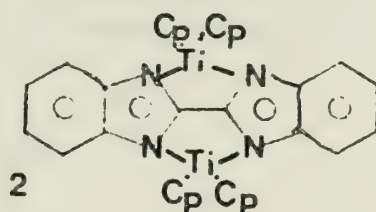
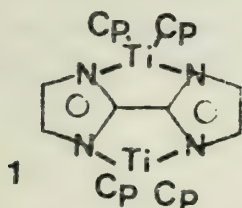
Benjamin Fieselmann

(Final Seminar)

March 31, 1977

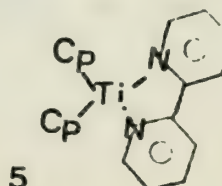
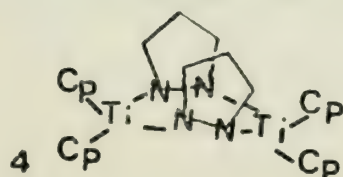
The study of low valent early transition metal compounds has been of increasing interest because of their ability to catalyze reactions such as the reduction of nitrogen to ammonia and the isomerization of olefins.^{1,2} Although reduced forms of titanium and vanadium tend to be reactive, especially with air, we have synthesized several thermally stable monomeric, dimeric, and trimeric low valent compounds which allowed us to study steric and electronic features and to better define the requirements for thermal stability.

Two different dimeric compounds were prepared by complexing two bis(cyclopentadienyl)titanium(III) units each to 2,2'biimidazole(1) and 2,2'bibenzimidazole(2). The variable temperature magnetic susceptibility of these two compounds showed antiferromagnetic coupling ($J = -25.2 \text{ cm}^{-1}$ and -19.2 cm^{-1} respectively). The small observed coupling here and in later compounds is fully consistent with the Alcock model and more recent ESR studies that place the d^1 electron in a largely nonbonding orbital between the cyclopentadiene rings.³ The ESR spectra for both dimers in the glass phase showed an $S=1$ triplet state spectra that can only be explained by the coupling of



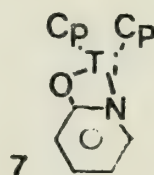
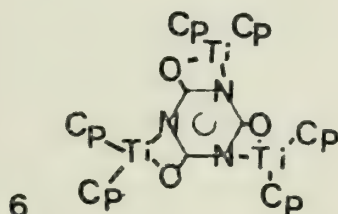
two adjacent spins.⁴ The monomer bis(cyclopentadienyl)titanium(III) methylbenzimidazole(3) was prepared and the ESR in the glass showed, in addition to titanium hyperfine ($A = 11\text{G}$), nitrogen hyperfine ($A = 2.2\text{G}$), which indicates delocalization of charge onto the bridge and suggests an exchange pathway through the bridge. The crystal structure of the titanium dimer of biimidazole confirms the dimeric structure and suggests that the chelate effect of the rigid bidentate bridge contributes to the thermal stability of the compounds.

A similar dimer was prepared where two bis(cyclopentadienyl)-titanium(III) groups are bridged by two pyrazole rings(4). Although the ESR spectrum is a typical $S = 1$ spectrum generated from interacting metal centers, the magnetic susceptibility shows no coupling down to the temperature of liquid helium. This lack of coupling could result from too small a J value to observe because of incorrect ligand orbital symmetry or from crystal packing forces in the solid which disrupt the coupling pathway. Single crystal X-ray structural studies indicate that the configuration of the dimer is that given below (4).



In 1976, E. O. Fischer⁵ reported one of the few stable organo-metallic titanium(II) compounds, bis(cyclopentadienyl)titanium(II) bipyridyl(5). In addition to its thermal stability, this d^2 compound is of interest because it has an anomalous magnetic moment of about .6 B.M. The magnetic moment can be explained successfully by showing that the molecule has a ground state singlet and an occupied excited triplet state. The solid state ESR intensity and the solution magnetic susceptibility determined by NMR (Evans Method)⁶ were both computer fit to theoretical expressions for singlet-triplet behavior that allowed calculation of the energy separation ($E = 758 \text{ cm}^{-1}$ in the solid state, 592 cm^{-1} in solution).⁷ The ESR in a glass shows a triplet spectrum indicating coupling between the electrons. The structure of the triplet state can best be described as a Ti(III) and a bipyridyl anion.

The structure of the isoelectronic d^2 compound bis(cyclopentadienyl)vanadium(III) monochloride was undertaken to provide further steric and electronic information on d^2 compounds. Unlike the dimeric monochlorides of bis(cyclopentadienyl) scandium and titanium, the vanadium compound is monomeric with the chlorine atom residing symmetrically in the open face of the tilted cyclopentadiene rings. The monomeric structure and paramagnetism (2.80 B.M.) can be explained by examining the molecular orbitals of the Cp_2V^+ moiety.⁸ A degeneracy between two orbitals results in two unpaired electrons. The symmetric structure results both from steric considerations and from electronic factors which attempt to minimize electronic repulsion between the ligand and metal.



Two trimers of cyanuric acid with three $\text{Cp}_2\text{Ti(III)}$ and three $(\text{MeCp})_2\text{Ti(III)}$ units have been synthesized (6). The trimers are thermally stable at over 250°C and have very intense molecular ion peaks in the mass spectra. The Ti(III) has a large enough atomic radius to form a four member ring and chelate with the oxygen and nitrogen atoms. The ESR spectrum in a glass can be interpreted as arising from both the populated quartet state and the doublet states.⁹ The magnetic susceptibility shows antiferromagnetic coupling and can be fit to a J value of $-.94 \text{ cm}^{-1}$. The monomer bis(cyclopentadienyl)titanium(III) 2-hydroxypyridine (7) shows an ESR signal unlike that of the trimer, which confirms that even with a very small coupling, the trimer's electronic structure is more complicated than just the sum of the properties of three independent monomers. The most likely pathway of exchange is a superexchange route through either the nitrogen or oxygen or both of the cyanuric acid.

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EXPERIMENTALLY DETERMINED RATES OF THERMAL ELECTRON TRANSFER IN MIXED-VALENCE IRON COMPOUNDS

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(Final Thesis)

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A mixed-valence compound typically contains two or more transition metal ions that are in different formal oxidation states.^{1,2} An electron(s) may, thus, be thermally transferred between transition metal ions. Experimental determinations of the rates of thermal electron transfer and development of a thorough understanding of the effects of chemical environments and changes in chemical environments on these rates are of interest. The insight gained from the investigation of simple mixed-valence compounds may be pertinent to understanding electron transfer processes in the biologically important class of compounds known as electron-transfer proteins.³

One type of mixed-valence compound investigated in this work is derived from μ -oxo-bis(tetraphenylporphinatoiron(III)), $[\text{Fe}(\text{TPP})]_2\text{O}$, and μ -oxo-bis(N,N'-ethylenebis(salicylideneiminatoiron(III))), $[\text{Fe}(\text{salen})]_2\text{O}$. These compounds are chemically oxidized to the corresponding oxo-bridged diiron(III,IV) compounds, $[\text{Fe}_2(\text{TPP})_2\text{O}]\text{X}$ and $[\text{Fe}_2(\text{salen})_2\text{O}]\text{X}$, where X^- is variously PF_6^- , BF_4^- , ClO_4^- or I_3^- . Antiferromagnetic exchange interactions are indicated in the variable temperature (4.2-267 K) magnetic susceptibility data which are least-squares fit to the theoretical equation for an isotropic exchange interaction ($\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$) in an $S_1 = 5/2$, $S_2 = 2$ dimer. The exchange parameters, J , for the $[\text{Fe}_2(\text{salen})_2\text{O}]\text{X}$ compounds are in the range of -7.5 to -17.6 cm^{-1} . Inclusion of an axial zero-field interaction, $D\hat{S}_z^2$, in the theoretical susceptibility equation for the $[\text{Fe}_2(\text{TPP})_2\text{O}]\text{X}$ compounds yields J values in the range of -83 to -119 cm^{-1} and $|D|$ -values in the range of 12 to 20 cm^{-1} .

A single, temperature-independent, quadrupole-split doublet is observed in the Mössbauer spectrum of each compound. No intervalence transfer band can be identified in the room temperature solution electronic absorption spectra of the $[\text{Fe}_2(\text{TPP})_2\text{O}]\text{X}$ compounds. Absorptions are observed at 450-500 nm in the electronic absorption spectra of the $[\text{Fe}_2(\text{salen})_2\text{O}]\text{X}$ compounds which are tentatively assigned as intervalence transfer bands. Isotropic EPR signals having g -values of ~ 2.0 are observed for the $[\text{Fe}_2(\text{salen})_2\text{O}]\text{X}$ compounds. The signals have temperature-dependent line widths. Either a high-spin Fe(III) or no EPR signal is observed for the $[\text{Fe}_2(\text{TPP})_2\text{O}]\text{X}$ compounds. These data indicate that the rates of thermal electron transfer are on the order of $\sim 10^{10} \text{ sec}^{-1}$ for these oxo-bridged diiron(III,IV) compounds.

Magnetic exchange interactions and electron transfer through the conjugated system of a porphyrin ring have been investigated by the synthesis of a four-iron containing compound, meso-tetraferrocenylporphyrin, H_2TFcP , its copper complex, $\text{Cu}(\text{TFcP})$, and the corresponding oxidation products, $[\text{H}_2\text{TFcP}](\text{X})_3$ and $[\text{Cu}(\text{TFcP})](\text{X})_2$ where X^- is variously I_3^- or DDQH^- , the hydroquinone anion of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. No magnetic exchange

interactions are indicated in the variable-temperature (4.2→270 K) magnetic susceptibility data for the $[\text{H}_2\text{TFcP}](\text{X})_3$ and $[\text{Cu}(\text{TFcP})](\text{X})_2$ compounds. Typical ferricenium magnetic susceptibility data are obtained. No intervalence transfer bands can be identified in the electronic absorption spectra and EPR signals typical of ferricenium ions are observed.

Variable-temperature (4.2→300 K) Mössbauer spectra of the $[\text{H}_2\text{TFcP}](\text{X})_3$ and $[\text{Cu}(\text{TFcP})](\text{X})_2$ compounds consist of two quadrupole-split doublets that correspond to the ferrocene and ferricenium centers. Relative area ratios of the two doublets are temperature-dependent. As the temperature decreases, the ferrocene to ferricenium area ratio increases. The loss of the ferricenium center results from unpaired electron density migration from the ferricenium centers to the porphyrin ring. Unpaired electron density migration is postulated to occur when the dihedral angle between the plane of the porphyrin ring and the substituted cyclopentadienyl ring of the ferricenium center approaches 0° . This allows the π -systems of the two rings to strongly interact. The temperature dependence is, possibly, the result of temperature dependent changes of the dihedral angle caused by crystal lattice packing rearrangements which are induced by counterions in the lattice.

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THE ADSORBENT AND THE ADSORBATE: APPLICATION OF EPR TO CATALYSIS

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April 12, 1977

Introduction

Since free radical intermediates are postulated in many catalytic mechanisms¹ and since many of the commercially important catalysts are supported transition metal ions,² the technique of electron paramagnetic resonance should be a useful tool in the study of catalytic processes. Due to its high sensitivity, it provides a unique technique for studying low concentrations of adsorbed intermediates and active sites. Epr spectroscopy is useful in unraveling the important aspects of catalysis on surfaces; the nature of the adsorbate and adsorbent and possible intermediates and mechanisms involved in the catalytic process. Several reviews have appeared in the literature.³⁻⁷

Application

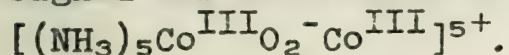
Transition Metal Ions. The chromia/silica system is an effective catalyst for polymerization of ethylene. It is believed that Cr^{5+} is the active ion in the catalytic process. Epr^{8,9} was used to study the nature of the active species. Cr^{5+} in a tetrahedral environment acts as a precursor to the active species which is thought to be a square-pyramidal complex that does not show an epr signal due to strong spin-lattice relaxation.

Nicula and coworkers¹⁰ studied the epr of Cu^{++} ions in CuY zeolites. The two main objectives were to study the effect of the number of Cu^{++} ions per unit cell and the level of dehydration on the epr signal. Systems with four Cu^{++} ions per unit cell showed an isotropic single line at room temperature and an anisotropic signal with hyperfine structure at high temperatures. The authors explain their results in terms of a tumbling effect of Cu^{++} ions in the fully hydrated zeolites versus a limited tumbling in the partially dehydrated systems.

Migration of metal ions in zeolites is a very interesting property that might be important catalytically. Using epr, it was possible to probe the migration of Cu^{++} ions in CuMg, CuZn, and CuLa exchanged Y-type zeolites.¹¹

Formation of fully coordinated complexes within the large cavities of zeolites where the framework oxygens need not be in the first coordination sphere of the metal ion provides a new role for zeolites as coordination catalysts. Lunsford and Vansant¹² were able to stabilize penta- and hexacoordinate Co(II)-methyl isocyanide in Co(II)CaY zeolites. Line shape of the epr signal, hyperfine due to ^{59}Co ($I = \frac{7}{2}$), and superhyperfine due to ^{13}C in $\text{CH}_3\text{N}^{13}\text{C}$ were used to detect the nature of the species and its ground state.

The reversible uptake of oxygen by Co(II) complexes in solution has been extensively studied, particularly with a view to understanding the bonding of oxygen in biological oxygen carriers. Prolonged exposure of ammoniated CoY zeolite to molecular oxygen results in an epr signal that shows 15-line hyperfine structure due to the interaction of the unpaired electron with two cobalt centers.¹³ The signal was attributed to μ -superoxo Co(III) dimer cation:



Adsorbed Species. The most studied adsorbed species is oxygen and the radicals formed from it on surfaces, namely, O_2^- , O^- and O_3^- . Conclusive evidence for the formation of O_2^- was obtained by observing the epr signal of an ^{17}O ($I=5/2$) enriched sample on γ -irradiated MgO .¹⁴ An eleven-line hyperfine pattern was seen in the spectrum as expected for a diatomic species with both labeled oxygen atoms. The equivalent ^{17}O hyperfine value of 77G indicates that O_2^- is interacting with the surface in a side-on fashion. A peroxy-type of bonding of O_2^- was detected by the epr of ^{17}O enriched O_2 on a decationated zeolite and Mo(VI) supported on silica gel.¹⁵ Two sets of six equally spaced hyperfine lines were observed, indicating that O_2^- with one labeled oxygen is formed where, in one case, ^{17}O is bonded to the surface and, in another, it is not.

Lunsford and Wang¹⁶ observed a 6-line hyperfine pattern in the spectrum of O_2^- on γ -irradiated NH_4Y zeolite and concluded Al ($I=3/2$) is the Lewis acid site and there is only one type of Al interacting with O_2^- on the surface.

By adsorbing ^{13}CO on Thoria,¹⁷ two types of CO adsorbates were detected by the observation of two sets of four hyperfine lines centered around g_{11} . From spin density calculations and conductivity measurements, it was concluded that chemisorption of CO results in the formation of slightly positive CO adsorbates and surface becoming slightly negative.

Contact of CO with TiO_2 with pre-adsorbed oxygen results in the formation of the species $[\text{O}_\text{I}-\text{O}_\text{II}-\text{CO}_\text{III}]^-$ whose identification was made feasible by observing hyperfine patterns due to ^{13}C and ^{17}O in an enriched sample.¹⁸ The magnitude of the ^{17}O hyperfine coupling constant increases in going from O_III to O_I . This is explained in terms of the species bonded to the surface^I at O_III pulling most of the negative charge towards the surface.

Recently,¹⁹ sulfur dioxide anions were formed in NH_4Y zeolites at 200°C . The analysis of the line shape of the epr signal as a function of temperature, time at constant temperature, and adsorbed O_2 pressure led to proposing that SO_2^- occurs at two sites, A and B, in the zeolite. Site A is located in the supercage and Site B might be located in the sodalite unit (most probably Site I).

Whereas other physical techniques probe extensively, one aspect of the catalytic process electron paramagnetic resonance has proven successful in probing both the adsorbent and the adsorbate. The most serious limitation of epr is that not all catalytic reactions involve paramagnetic species; or, even when they do, these species might be undergoing strong spin-lattice relaxation that renders their detection very difficult.

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Reactions of the Unsaturated Cluster $\text{H}_2\text{Os}_3(\text{CO})_{10}$
With Lewis Bases and Olefins

Jerome Keister

April 28, 1977

Metal carbonyl clusters have been the object of increasing interest in recent years due to their potential as unique homogeneous catalysts, for novel reactions in which more than one metal center may participate, and for models for the active sites of metal surface catalyzed reactions.¹ However, although many reactions of clusters have been described, very little is known about their mechanisms due to the severe conditions required to induce reactivity with saturated clusters. The reactions of $\text{H}_2\text{Os}_3(\text{CO})_{10}$, a triangular cluster with a formal metal-metal double bond, have been studied because its much higher reactivity allows reactions to be carried out under mild conditions and mechanisms can be examined in detail.

Dihydridodecacarbonyltriosmium reacts with Lewis bases, including carbon monoxide, phosphines, phosphites, arsines, pyridines, isocyanides, and halides, to form complexes $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{L}$.² These adducts each have one terminal and one bridging hydride, which undergo intramolecular exchange with a free energy of activation dependent on the donor properties of L. The mechanism involves a pseudo-four-fold rotation of the two hydrides, one axial carbonyl, and one equatorial carbonyl, all on the same metal atom. The adducts $\text{H}_2\text{Os}_3(\text{CO})_{10}(\text{CNR})$ (R=Me, CH_2Ph , tBn) undergo intramolecular rearrangement to $\text{H}_2\text{Os}_3(\text{CNHR})(\text{CO})_{10}$, which have both the hydride and C=NHR group bridging one edge.

Reactions of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ with 1-alkenes form $\text{H}_2\text{Os}_3(\mu\text{-CH=CHR})(\text{CO})_{10}$ and one equivalent of the corresponding alkane.³ With fumarate esters, the intermediates $\text{H}_2\text{Os}_3[\text{CH}(\text{CO}_2\text{R})\text{CH}_2\text{CO}_2\text{R}](\text{CO})_{10}$ can be isolated and characterized. Alkyls can also be isolated from reactions with acrylates and maleic anhydride and with ethyl diazoacetate the complex $\text{H}_2\text{Os}_3(\text{CH}_2\text{CO}_2\text{Et})(\text{CO})_{10}$ is isolated. These alkyls decompose in the presence of 1-alkenes to form the saturated ester and the corresponding $\text{H}_2\text{Os}_3(\mu\text{-CH=CHR})(\text{CO})_{10}$. In the presence of H_2 the decomposition forms $\text{H}_2\text{Os}_3(\text{CO})_{10}$ and the saturated ester. Thus, $\text{H}_2\text{Os}_3(\text{CO})_{10}$ is a catalyst for the hydrogenation and isomerization of 1-alkenes.⁴

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THE REACTIONS OF UNSATURATED TRIOSMIUM
CARBONYL CLUSTERS

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(Final Thesis)

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Due to the severe conditions necessary to dissociate carbon monoxide from the parent molecule, most of the previously known triosmium carbonyl complexes derived from the reactions of $\text{Os}_3(\text{CO})_{12}$ with organic molecules were already thermally stable, ¹ i.e., isolation of conceivable intermediates was very difficult. Use of the electronically unsaturated cluster $\text{H}_2\text{Os}_3(\text{CO})_{10}[\text{I}]$ as the starting material made it possible to prepare otherwise unisolable thermally unstable complexes.²

From the reactions of $[\text{I}]$ with a number of 1,3-dienes, compounds of the formula $\text{Os}_3(\text{CO})_{10}(\text{diene})$ were isolated. Depending on the positions of substitutions of the dienes, s-cis-1,3-dienes on one osmium as well as s-trans-1,3-dienes on two osmiums of the triosmium unit were produced from this reaction. Of the molecules having coordinated s-cis-1,3-dienes, again depending on the positions of the substitution, some take axial-equatorial, and others take "capped" coordination on one osmium center. 1,3-butadiene, which is the simplest 1,3-diene, afforded all three of the possible forms of coordination, and the two s-cis-diene isomers were found to be exchanging on the nmr time scale.³

Reactions of acetylenes with $[\text{I}]$ yielded a variety of deca- and nona- carbonyl triosmium complexes. Of particular interest among them were $\text{Os}_3(\text{CO})_{10}(\text{PhC}_2\text{Ph})$ from diphenylacetylene, and, a series of osmiacyclohexadienone complexes, $\text{Os}_3(\text{CO})_9(\text{C}_4\text{H}_2\text{R}_2\text{CO})$'s, $\text{R} = \text{Et}$. The former was shown to lose carbon monoxide by heating to form $\text{Os}_3(\text{CO})_9(\text{PhC}_2\text{Ph})$, which reacted with another molecule of diphenyl acetylene, resulting in an unstable $\text{Os}_3(\text{CO})_9(\text{PhC}_2\text{Ph})_2$ compound that rearrange into a known osmium cluster $\text{Os}_3(\text{CO})_9(\text{C}_4\text{Ph}_4)$, which could be obtained from the reaction of $\text{Os}_3(\text{CO})_{12}$ with diphenylacetylene. This demonstrated the presence of three intermediates between the starting compound $\text{Os}_3(\text{CO})_{12}$ and the final product $\text{Os}_3(\text{CO})_9(\text{C}_4\text{Ph}_4)$.⁴ The series of compounds from the reaction of ethylacetylene and $[\text{I}]$, of three isomeric form $\text{Os}_3(\text{CO})_9(\text{C}_4\text{H}_2\text{Et}_2\text{CO})$, underwent thermal decomposition to give, depending on the position of ethyl substitution, cyclopentadienyl-, and cyclopentadienone- compounds with oxidatively added methylene C-H bonds. These reactions appeared to proceed via unsaturated intermediates of the formula $\text{Os}_3(\text{CO})_9(\text{diethyl cyclopentadienone})$.

The reaction of $[\text{I}]$ with ethylene in cyclooctene resulted in a high yield of the labile complex $\text{Os}_3(\text{CO})_{10}(\text{C}_8\text{H}_{14})_2[\text{II}]$, which could be converted to the slightly more stable $\text{Os}_3(\text{CO})_{10}(\text{NC-CH}_3)_2$ complex $[\text{III}]$ quantitatively.⁵ Starting from $[\text{II}]$, a large number of $\text{Os}_3(\text{CO})_{10}\text{L}_2$ compounds ($\text{L} = \text{phosphines, phosphites, nitriles, and isonitriles}$), and $\text{HOs}_3(\text{CO})_{10}\cdot\text{X}$ compounds ($\text{X} = \text{OR, NHR, Cl, Br, SR, and H}$) were prepared in high yield under mild conditions.

Under somewhat more severe conditions (50-80°C, 10 min.), [III] reacted with a number of nonconjugated dienes, affording $\text{Os}_3(\text{CO})_{10}(\text{diene})$ compounds (diene = 1,5-COD, NBD, bicyclooctadiene, 1,5-hexadiene, and, tetrafluorobenzobicyclooctatriene) in good yield.⁶ Under similar conditions, oxidative addition reactions of the C-H bonds of various substrates proceeded with the bis-acetonitrile complex. Thus, the reactions of pyridine,⁷ acetophenone, and, acetaldehyde resulted in $\text{HOs}_3(\text{CO})_{10}\cdot\text{X}$ complexes (X = 2-pyridyl, 2-acetylphenyl, and acetyl). Another type of reaction of [III] was the dehydrogenation of alkyl amines resulting in the formation of [I] and $\text{HOs}_3(\text{CO})_{10}(\text{amine-3H})$ compounds (amine = triethyl amine, pyrrolidine, and piperidine).

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Determination of Thermodynamics of Acid-Base Reactions Using Gas-liquid Chromatography (glc)

Craig S. Chamberlain

Final Seminar

June 21, 1977

One approach to understanding the reactivities of transition metal complexes is to determine and correlate thermodynamic parameters for reactions between metal complexes(acids) and ligands(bases).¹ However, these parameters are not always easily determined by conventional techniques when the ligand is gaseous, the metal complex air sensitive or available only in small amounts, or when more than one ligand tends to coordinate to the metal complex.² For this reason, the glc method has been investigated as a complimentary alternative to the other techniques.

The basic glc expression for the equilibrium constant for the simple reaction $A + B \rightleftharpoons A-B$ is given by³

$$K_1 = \left(\frac{K_R}{K_R^0} - 1 \right) \frac{1}{[A]}$$

where K_R is the volume of carrier gas required to elute the injected ligand from a column containing 1.0 ml of a solution of complex of concentration $[A]$ and K_R^0 the elution volume for a solvent column. ΔH and ΔS are determined by varying the temperature of the experiment, i.e., $-R \ln k_1 = \frac{\Delta H}{T} - \Delta S$. Contributions to the observed K_R values from interactions of the ligand at the liquid and solid surfaces must be eliminated by one of several methods⁴, yielding fully corrected values.

The basic theme of the investigations described below is the determination of (1) the validity of the various glc methods, (2) the limitations of same, and (3) modifications necessary to make the methods applicable to systems involving metal complexes.

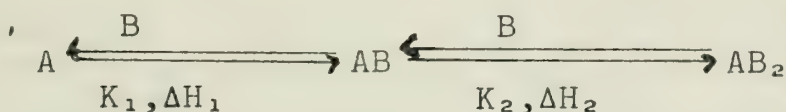
A gas chromatograph was constructed and interfaced to an IBM Systems 1800 computer. The neat base on column method⁵ was tested by determination of enthalpies for several hydrogen bonding systems using both glc and alternate techniques.⁶ Good agreement was found between the two sets of data, verifying the validity of this glc method.

To determine if gaseous reactants would present problems the glc enthalpy for sulfur dioxide and di-n-octyl ether was determined. There is good agreement between this and that calculated using the E and C equation.¹ A Schlenk type apparatus has been designed and tested which allows one to place air sensitive compounds on the glc column without decomposition.

The solution on column method³ was then tested since it is the method of choice for transition metal complexes. However, it has never been coupled with fully corrected K_R values and no comparison of enthalpies obtained by this and other methods has been made. Spectroscopic and glc thermodynamic measurements for the interaction between bis(7,7,11,11-tetramethyl heptadecane-8,10-dionato)nickel(II) and triethyl amine were made, the enthalpies being in very good agreement. Several authors have reported discrepancies between glc and other types of equilibrium constants⁷, but in this study the two sets agreed fairly well. During this work a simplified graphical technique of obtaining fully corrected data was discovered which now makes the glc technique available to workers with access to a research grade chromatograph.

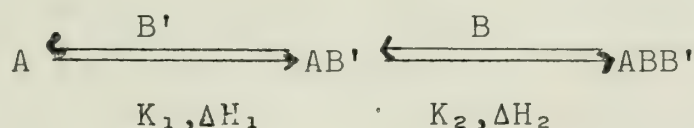
Several transition metal complexes have been prepared for this work which have the unusual property of being high molecular weight liquids at room temperature.

Difficulties are encountered using conventional techniques to determine thermodynamic parameters for the first step in multi-step systems of the type



because of contributions from the second step.² Bis(di-n-octyl-dithiophosphato) nickel(II) will coordinate two moles of pyridine. Basic glc equations indicate that only contributions for the first interaction should be seen on the glc if small injection volumes of base are used. The glc enthalpy was obtained using this method. It compared well to the ΔH_1 reported for essentially the same system obtained by a spectrophotometric method.⁶ Thus it appears that glc can be used to obtain ΔH_1 for systems of this type.

The above studies indicate that glc is a reliable technique which is applicable to difficult systems. Based on the characteristics of the glc technique a plan is proposed to determine the enthalpies for the second step of the following interaction for a number of non-volatile bases B':



This information would allow one to learn more about how B' effects the acidity of AB' towards B. This is, of course, important in certain catalytic and biological systems.

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Amine-Chelated Lithio Cyclopentadienyl
Transition Metal Complexes

Robert Mink

(Final Seminar)

August 19, 1977

Organolithium chemistry has experienced a rapid growth in recent years due to the large synthetic utility shown by the reagents. In many situations, organolithium reagents are becoming preferred to Grignard reagents. Studies have shown that the reactivity of an organolithium compound increases greatly when the lithium atom is complexed with tertiary polyamines, the most common being N, N, N', N'-tetramethylethylenediamine (TMED).

The metalation of ferrocene using n-butyllithium yields a mixture of the mono- and dilithio complexes. Pure monolithioferrocene can only be prepared from a substituted ferrocene. In the presence of a chelating agent such as TMED or 1, 1, 4, 7, 7-pentamethyldiethylenetriamine (PMDT), the metalation of ferrocene produces pure amine-chelated dilithioferrocene. The X-ray structure and NMR spectra of dilithioferrocene·PMDT confirm the presence of only one PMDT moiety per two lithium atoms. NMR data indicates that this compound exhibits stereochemical nonrigidity with the structure in solution identical to the solid state structure at low temperatures. From the NMR spectra it was determined that two exchange processes are occurring; one involving the PMDT and cyclopentadienyl rings and the second involving the PMDT only. The mechanism suggests an attack of PMDT from the solvated to the unsolvated lithium atom. At higher temperatures the PMDT completely dissociates.

It was found that the base PMDT is more advantageous than TMED because of the greater solubility in aromatic solvents of the resulting amine-chelated lithio transition metal complexes. The metalation of $(C_5H_5)_2ReH$ using n-butyllithium and PMDT produces $(C_5H_5)_2ReLi \cdot PMDT$, where lithiation has occurred at the metal atom rather than the cyclopentadienyl ring as in ferrocene. The rhenium-lithium complex reacts with carbon monoxide, carbon dioxide, water, and hydrogen. The treatment of $(C_5H_5)_2ReLi \cdot PMDT$ with alkyl halides leads to the formation of $(C_5H_5)_2ReR$ (R = alkyl) complexes, which show high thermal stability. The reaction of $(C_5H_5)_2ReLi \cdot PMDT$ with organometallic halides yields dimetallic complexes in which a metal-metal bond is formed. Two of the dimetallic compounds also contain a bridging carbonyl group.

Addition of n-butyllithium and PMDT to bis(cyclopentadienyl)-molybdenum dihydride affords bis(cyclopentadienyl)hydrido (1, 1, 4, 7, 7-pentamethyldiethylenetriaminelithio)molybdenum. The PMDT·lithio tungsten analog has also been prepared but, like the TMED·lithio cyclopentadienyl transition metal complexes, it is insoluble in aromatic solvents. Both the molybdenum-lithium and tungsten-lithium intermediates react with carbon monoxide, carbon dioxide, hydrogen, and alkyl halides.

Theoretical Investigation of Homogeneous Ziegler-Natta Catalysis

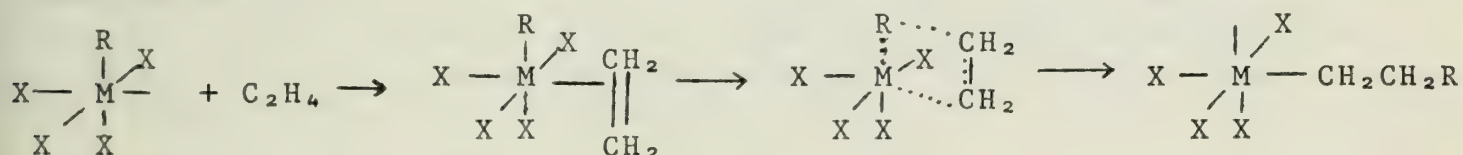
David R. Gard

October 11, 1977

Introduction

Ziegler's report¹ in 1954 that ethylene could be polymerized at atmospheric pressure and ambient temperature to a linear, high molecular weight polymer with a combination transition metal-metal alkyl catalyst opened an entirely new field of catalysis. Other workers² have considerably extended this reaction, in particular Natta,² whose control of the stereoregular polymerization of α -olefins with Ziegler catalyst systems has led to wide industrial application.

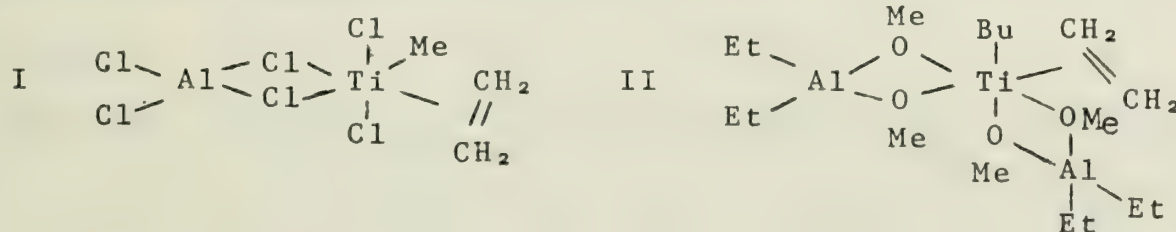
There have been numerous suggestions³ proposed as to the mechanism of Ziegler-Natta catalysis, but due to the diversity and complexity^{4,5} of these systems many of these ideas are of limited benefit. Nevertheless, a great number of experimental investigations have revealed the most fundamental features.⁴ The mechanism proposed by Cossee⁶ concurs most fully with the experimental data and has received wide acceptance.^{7,8} This mechanism involves alkylation of the transition metal center followed by olefin coordination to an octahedral vacant site and cis-migration of the alkyl group to the olefin through a concerted, four-centered transition state:



The Cossee mechanism is essentially qualitative, but recently some theoretical studies have been performed in order to examine quantitatively the electronic structure of the proposed intermediates.

Chain Propagation via Insertion

Armstrong⁷ and Novaro⁹ have conducted SCF-CNDO-MO, all valence electron calculations of the electronic structure of model soluble catalyst-olefin complexes, (I) and (II):



The changes in charge distribution and molecular orbital energies and character over the course of the reaction support Cossee's overall conception of insertion as the mechanism of chain propagation in Ziegler-Natta catalysis. However, certain points of disagreement arise which afford a better understanding of the process. The bond order of the titanium-olefin π -backdonation component = ~ 0.01 for (I). This casts doubt upon Cossee's proposal that stabilization of the titanium ' t_2 ' orbital is a prerequisite for the activation of the titanium-alkyl bond. Hence, the driving force is not prior activation of the titanium-alkyl bond, but a substantial lowering of the energy barrier to alkyl insertion through proficient mixing of the alkyl σ and olefin π^* orbitals via the ' t_2 ' orbital. The titanium-alkyl bond is quite polarized, with a charge on the titanium atom of +1.17 for (I) and on the alkyl α -carbon atom of -0.24 and ~ 0.30 for (I) and (II) respectively. The olefin has an overall slight positive charge and the reaction is initiated by the interaction between the olefin and the alkyl group in the catalyst-olefin complex. Only minor changes in the orbital energies occur during the insertion reaction, with the substrates remaining bonded to the titanium atom at all times. The catalytically active complex is trigonal bipyramidal before olefin coordination, and not octahedral with a vacant site. This has been confirmed by EPR^{9,10} and by further calculations on (II).¹¹

Unsymmetrically substituted ethylenes with weakly polar double bonds such as propene or styrene exhibit predominately Markovnikoff insertion with titanium-alkyl bonds. With Group VIII metal based catalysts, however, a pronounced tendency for anti-Markovnikoff insertion is observed.¹² This regioselectivity can be explained using the orbital overlap model of Armstrong,⁷ which considers the relative shifts in population of the olefin π and π^* orbitals upon coordination to the catalyst complex.

Catalyst Tailoring and β -Hydrogen Transfer

Tailoring of Ziegler-Natta catalysts to develop polymers of desired molecular weight, degree of branching, or possession of unsaturated groups depends mainly upon control of β -hydrogen transfer at the transition metal center, as this reaction can bring about termination or isomerization of the growing polymer chain.¹³ Novaro has attempted to show that β -hydrogen transfer between ~~metal center~~ olefin and alkyl group and insertion stem from the same initial situation and that interaction of an alkyl group and an olefin on a titanium center can lead to either reaction.

Conclusion

Molecular orbital calculations have complemented the diverse experimental data in providing insight into the nature of Ziegler-Natta catalysis. The Cossee mechanism has gained feasibility but more work of this type needs to be done to differentiate between alternative intermediates and mechanisms both for Ziegler-Natta and for other catalytic systems.

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RECENT DEVELOPMENTS IN THE STUDY OF ISONITRILE INSERTION REACTIONS

Daniel S. Foose

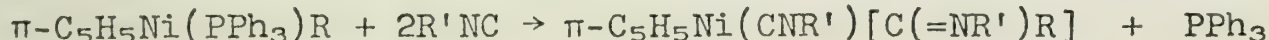
October 18, 1977

The insertion reaction is one of the most important reactions in organometallic chemistry. This type of reaction is one that conforms to the general equation

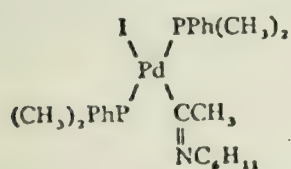


where M is a metal and X and Y are monatomic or polyatomic species. The recent growth of interest in these reactions stems from the realization that homogeneous catalytic reactions, such as hydroformylation or polymerization, proceed by one or more insertion steps. In addition, many insertion reactions have been successfully employed in organic and organometallic synthesis. The insertion of isonitriles into metal-carbon bonds was first reported by Yamamoto, et al.¹ in 1968. The large amount of work that appeared in the years immediately thereafter has been reviewed.^{2,3,4} Recent investigations have been concerned with isonitrile insertions into metal-carbon, metal-hydrogen, metal-halogen and metal-metal bonds.

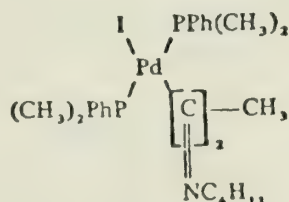
Isonitriles are known to insert into metal carbon bonds involving nickel, palladium, platinum, iron, molybdenum and manganese. The first isonitrile insertion products obtained^{1,5} were π -cyclopentadienyl (cyclohexylisonitrile)[alkyl(cyclohexylimino)methyl] nickel.



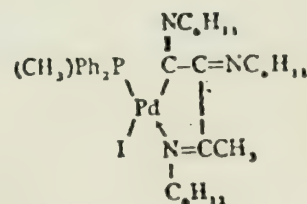
No intermediate was isolated and the mechanism of the reaction was not ascertained. Several other examples of both single and multiple isonitrile insertions have since been reported. The complex trans-iodobis(dimethylphenylphosphine)methyl palladium is known to undergo both single and multiple insertions into the palladium-carbon bond⁶ to produce products of types I, II, and III. Recent studies⁷ of related



I



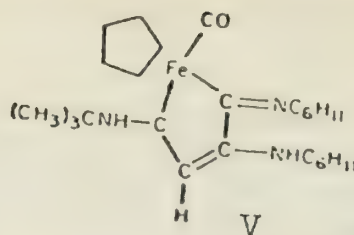
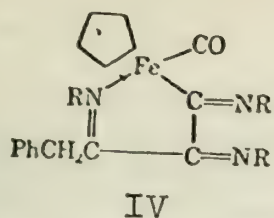
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III

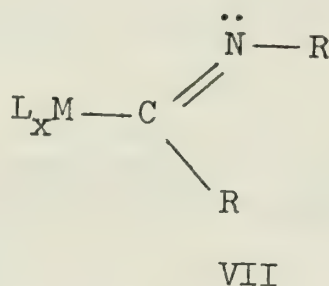
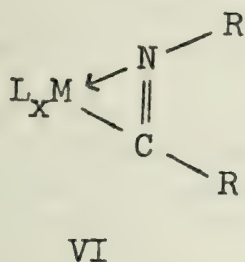
compounds have shown that the steric effect of the phosphine, isonitrile, or alkyl ligands seems to be an important factor in the control of reactivity, for both multiple insertions as well as single insertions. Other investigations of palladium-carbon insertions include the reactions of dimethyl- and diphenyl-mercury with dihalobis(isonitrile) palladium complexes to produce bis(imino) compounds⁸ and a study of the mechanism and stereochemistry of insertion into metal alkyl and vinyl bonds in square planar complexes.⁹ Multiple insertion products have been obtained with the direct reaction of isonitriles with dicarbonyl- π -cyclopentadienylalkyliron. Structure IV was proposed as a possible

structure for the triple insertion product.¹⁰ A revised structure¹¹

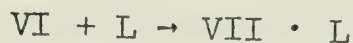


for this "trisimino-type complex" has recently been reported. X-ray structural determination has revealed a novel type of chelating carbene (structure V).

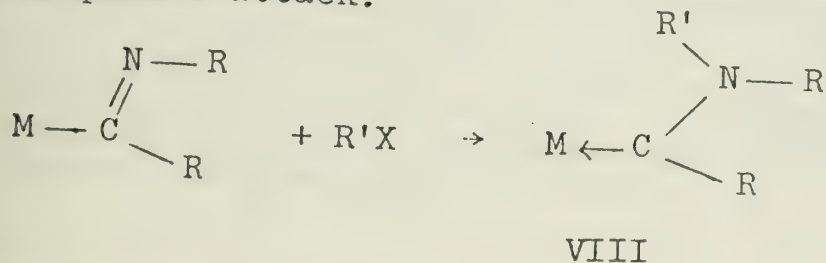
Insertion into the metal-carbon bonds of molybdenum and manganese has been obtained from the reactions of anionic organometallic complexes of the general type $L_x(CNR)_yM^-$ with alkyl halides.¹² Complexes that contain a novel 'dihapto' iminoacyl ligand (VI) have been produced.



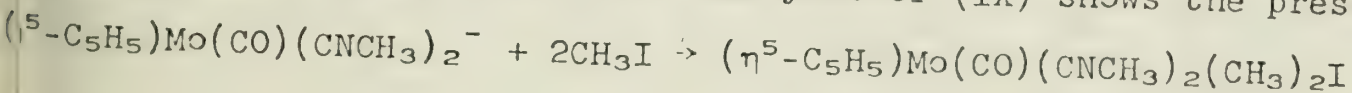
It was observed that these dihapto complexes readily react with donor ligands to form adducts, which contain normal monohapto iminoacyl ligands (VII).¹³



In effect, complexes containing the dihapto ligand act as if they are coordinately unsaturated by virtue of this facile dihapto-monohapto transformation. An interesting feature of the η' -iminoacyl (VII) is that it contains a lone pair on that nitrogen atom that is susceptible to electrophilic attack.



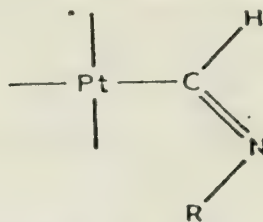
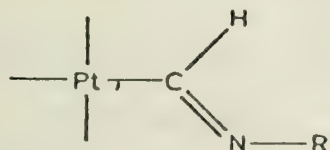
Protonation or alkylation at this site leads to the formation of molecules containing the aminocarbene ligand (VIII). The presence of two isonitrile ligands in the coordination sphere of the metal atom permits the occurrence of multiple isonitrile insertion rearrangements.¹³ X-ray structural analysis of (IX) shows the presence



IX

of a polyhapto ligand that can be described as an iminodimethyl-aminocarbene.

Insertions of isonitriles into metal-hydride bonds have been reported for complexes of platinum.^{14,15} The complex $\text{trans-[PtH(CNR)(PEt}_3\text{)]Cl}$ undergoes insertion into the platinum-hydride bond to afford complexes containing the formimidoyl ligand. Spectroscopic



data on the complex with R=p-tolyl showed the presence of two isomers, arising from different orientations of the p-tolyl group about the carbon nitrogen double bond. Protonation or alkylation of the nitrogen atom of the formimidoyl complexes affords relatively uncommon cationic secondary carbene products.

Isonitriles were earlier shown to insert into the metal halogen bonds of niobium and tantalum halide complexes.¹⁶ These insertions have recently been extended to include the halide complexes of titanium, zirconium, hafnium and vanadium.¹⁷

Recent examples involving the insertion of isonitriles into metal-metal bonds are the reactions of isonitriles with $[\text{Pd}_2(\text{CNCH}_3)_3]^-$ $[(\text{C}_6\text{H}_5)_2]_2[\text{PF}_6]_2$ and $[\text{Pt}_2(\text{CNCH}_3)_3]^-$ $[(\text{C}_6\text{H}_5)_2]_2[\text{PF}_6]_2$.¹⁸ The most conspicuous feature of this reaction is the expansion of the metal-metal distance which occurs upon the formation of these bridging isonitrile complexes.

Conclusion:

The increasing number of reports of isonitrile insertions into metal-carbon, metal-hydrogen, metal-halogen and metal-metal bonds seems to indicate the generality of this reaction in organometallic chemistry. Recent investigations have shown the importance of steric control in both single and multiple insertions. Study of the reactivity of isonitrile insertion products, e.g., the dihapto iminoacyl complexes, may provide us with an increased understanding of the overall course of isonitrile insertion reactions.

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ESR AND THERMODYNAMIC STUDIES OF THE REACTION BETWEEN COBALT(II)
 PROTOPORPHYRIN IX DIMETHYLESTER AND DIOXYGEN

John Breese

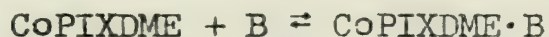
(Final Seminar)

October 20, 1977

The oxidation of organic substrates by molecular oxygen is an extremely important class of chemical transformations. The conversion of petroleum-based chemicals to useful chemical intermediates by controlled oxidation is a major concern of the chemical industry. Likewise, the inhibition of the oxidative decomposition of numerous "finished products" such as plastics, lubricating oils, paints, and rubber is of equal importance. Catalysis of the first process and inhibition of the latter by transition metal complexes have both been areas of considerable technological interest.¹⁻⁵

In this study a systematic determination of the factors important in the binding and activation of dioxygen by a transition metal complex was undertaken. Also the electronic perturbation that the binding of O₂ has on the metal center was considered. Cobalt (II) complexes are particularly well qualified for understanding the electronic nature of the metal-O₂ interaction as they have at least one unpaired electron, making them ESR active, and, in many geometries, an unpaired electron resides in the orbital to which the dioxygen binds. The ESR analysis of the cobalt-dioxygen complexes has been the source of some speculation and debate in the literature.⁶⁻¹⁰ Initially, it was hoped that this study would shed some light on many of the present misconceptions.

Cobalt (II) protoporphyrin IX dimethylester (CoPIXDME) was the complex chosen for this study. The enthalpies for dioxygen binding to this complex as a function of base have previously been reported.^{11,12} The enthalpy for the reaction



was measured for the bases 1-methylimidazole, pyridine, piperidine, and tetrahydrothiophene. A good fit to the E and C equation was obtained, which implies that π -backbonding is unimportant in these complexes. It was found that there is a direct relationship between the strength of base binding and the strength of oxygen binding.

The fractional electron transferred (E. T.) from the cobalt to the oxygen was measured as a function of axial base by a previously reported procedure.¹³ It was found that as the base-cobalt bond gets stronger the E.T. decreases, which is exactly the opposite behavior from that predicted by the "electron transfer model."¹⁴ This observation is explained by contributions from three mechanisms:

- 1) core polarization
- 2) indirect polarization arising from unpaired spin residing on the dioxygen fragment
- 3) mixing of the doublet ground state with the quarter excited state.¹⁵

By consideration of other cobalt-dioxygen systems, it is shown that the latter mechanism is the most important.

Oxidation studies utilizing 2,6-dimethylphenol indicate that as the base gets stronger (and supposedly the complex has more cobalt(III)-O₂⁻ character) the oxygen becomes more activated. However, a limit has been found for the base strength, after which irreversible oxidation of the metal is the dominant reaction.

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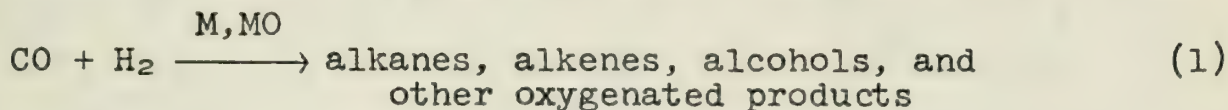
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HOMOGENEOUS CATALYSIS OF THE FISCHER-TROPSCH REACTION

William L. McCullen

November 1, 1977

For several years, the Fischer-Tropsch reaction¹ (eq. 1) has



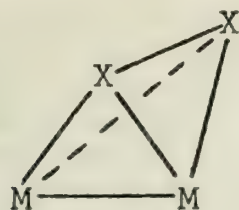
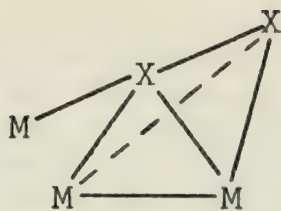
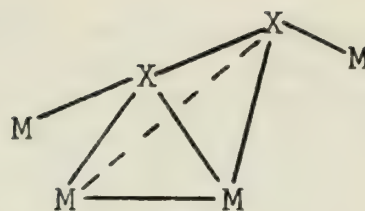
M, MO = transition metals and metal oxides

been employed in South Africa for the industrial production of a wide variety of useful organic products from synthesis gas, a mixture of CO and H₂ which is readily available from coal gasification.^{2,3} In this respect, coal could supplant crude petroleum as the source of raw material for production of industrial chemicals. However, industrial-scale implementation of the heterogeneous catalysis of the Fischer-Tropsch reaction suffers two major drawbacks. One undesirable feature is the lack of reaction specificity. In view of the variety of products obtained from the reaction shown in eq. 1, it is not surprising that the product distribution is quite sensitive to the CO/H₂ ratio, reaction conditions, and the selection of the metal catalyst. Despite stringent control of reaction parameters (temperature and pressure) and judicious choice of the catalyst, the synthesis generally yields several products. Difficulties in studying surface properties, chemisorption, and adsorbate properties have hampered attempts at determining the kinetics and mechanism of the heterogeneous process.³ Another significant disadvantage is the large energy requirement. Ordinarily, tremendous pressure (10-1000 atm.) and high temperature (150-500°C) are required to activate the metal catalyst. Such great energy expenses are becoming increasingly uneconomical with respect to the rising cost and availability of energy sources.

There is reasonable belief⁴ that homogeneous catalysis will provide greater product selectivity than heterogeneous methods with smaller energy requirements. However, metal surfaces exhibit certain properties with respect to an adsorbed species which should be preserved in the design of homogeneous catalysts.⁵ The possibility of multi-metal bonding interactions between the adsorbed species and the metal surface, and the apparent mobility of the adsorbate over the metal surface are two such properties which are probably crucial in the activation and subsequent reduction of carbon monoxide. Metal clusters have been proposed as a general class of compounds that might serve as effective homogeneous catalysts for the Fischer-Tropsch reaction.³⁻⁹

In designing systems for catalytic behavior, Muetterties has suggested the hypothesis that the susceptibility of CO to reduction should directly correlate with the degree of CO bond lengthening in the metal complex.⁹ As a consequence, increasing the number of metal-carbonyl interactions should lengthen the CO bond. Crystal structures of metal carbonyls show this to be generally true. However, the synthesis of hydrocarbons probably requires greater bond reduction than can be realized through any of the three normal modes of CO bonding for it involves the scission of the CO bond. (This is the strongest bond of any diatomic molecule.) To facilitate CO bond cleavage, the following

bonding modes have been proposed:⁹


 $\mu_2-\eta^2$

 $\mu_3-\eta^2$

 $\mu_4-\eta^2$

Crystallography has never revealed any of these bonding modes for metal carbonyl compounds, yet it is likely that such interactions may be involved in the transition state species of CO reduction processes. The $\mu_x-\eta^2$ ($x=1,2$) modes have been observed for various acetylenes in Ni_4 clusters and, in a few instances, reaction with H_2 resulted in the facile reduction of the coordinated acetylene to cis-olefins. Another important feature which suggests the selection of metal clusters as homogeneous catalysts is the well-established phenomenon of intramolecular ligand mobility. The oxidative addition of H_2 followed by hydride migration is probably an important sequence in CO hydrogenation; furthermore, CO migration is considered an essential step in the synthesis of compounds containing carbon-carbon bonds.

Survey of Homogeneous Fischer-Tropsch Systems

There have been several reports of homogeneous Fischer-Tropsch type reactions, in which the promoter or active catalytic species were proposed to be mono-metallic. Bercaw and co-workers¹³ reported the synthesis of methanol in a three step process promoted by a derivative of $[(\eta^5\text{-C}_5\text{Me}_5)\text{ZrN}_2]_2\text{N}_2$ generated in situ. Shoer and Schwartz¹⁴ observed the synthesis of a series of low molecular weight alcohols from CO and $(i\text{-C}_4\text{H}_9)_2\text{AlH}$ in a multi-step reaction promoted by Cp_2ZrCl_2 . Caulton and others¹⁵ reported that Cp_2TiCl_2 promoted the methanation reaction under mild conditions. However, the workers did suggest the possibility of a bimetallic species in the reaction mechanism. Petit¹⁶ reported the synthesis of methanol catalyzed by $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$. Unfortunately, few details are readily available for this reaction.

Undoubtedly, a great deal of research using metal clusters is being conducted but few results have appeared in the literature. Perhaps the most significant contribution to date is that of Pruett and co-workers in which they report the synthesis of ethylene glycol from CO and H_2 promoted by $\text{Rh}_4(\text{CO})_{12}$.¹⁷ Infrared work suggests that the clusters $[\text{Rh}_{12}(\text{CO})_{34}]^{2-}$ and $[\text{H}_5\text{-}\eta\text{-Rh}_{13}(\text{CO})_{24}]^n$ are the dominant reaction species.¹⁸ Muetterties and co-workers^{19,20} have reported homogeneous catalysis of the Fischer-Tropsch reaction with $\text{Os}_3(\text{CO})_{12}$ and $\text{Ir}_4(\text{CO})_{12}$ yielding low molecular weight alkanes under mild reaction conditions. The use of a molten salt medium and the addition of a particular Lewis acid has proven to be a more selective and efficient synthetic method than the use of organic solvent media. Though the reaction mechanisms for these systems are unknown, it is believed that interaction of the CO moiety with several metal centers in an asymmetric mode is responsible for the activation of the carbon-oxygen bond toward hydrogenation.

Summary

Homogeneous catalysis of the Fischer-Tropsch reaction should provide a more efficient and selective synthetic means of chemical production than heterogeneous catalysis, the method primarily used by industry today. The design of homogeneous catalysts should combine features of metal surfaces with the versatility of organo-metallic compounds. Metal clusters should provide such a class of compounds, and preliminary results indicate that some heavy metal clusters do exhibit catalytic behavior in the Fischer-Tropsch reaction. These findings are encouraging and have stimulated further research in this area.

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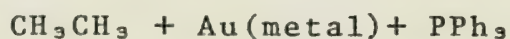
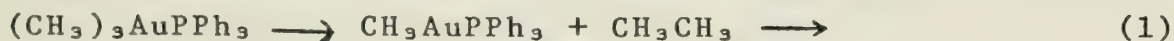
MECHANISTIC STUDIES OF ALKYL-ALKYL COUPLING

MEDIATED BY ORGANOGOLD COMPOUNDS

James J. Welter

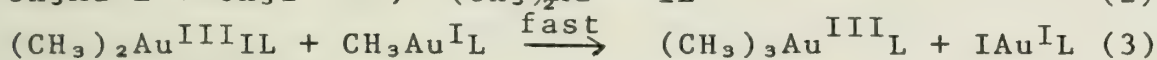
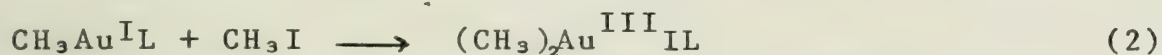
November 3, 1977

Organogold compounds^{1,2} were among the first organometallic species investigated during the 1860's.³ However, marked progress in the synthesis of organogold derivatives was not achieved until the 1900's by Gibson⁴ and Gilman.⁵ The discovery in 1963 that tertiary phosphines had a stabilizing effect on trimethylgold compounds led to the isolation of $(\text{CH}_3)_3\text{AuPPh}_3$.⁶ $(\text{CH}_3)_3\text{AuPPh}_3$ was found to decompose according to eq.(1).



The decomposition via coupling of the methyl groups sparked the present day interest in mechanistic studies of trialkyl gold complexes.

Alkyl groups on organogold complexes have been shown to couple with alkyl halides as shown below for CH_3AuL and CH_3I .⁷

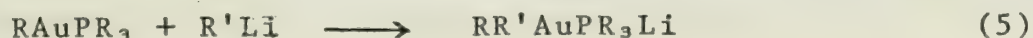


NMR studies have helped to elucidate the mechanisms of the oxidative addition, alkyl isomerization, and reductive elimination steps in this cycle.

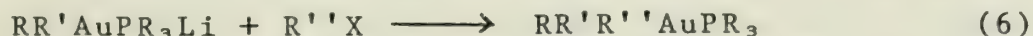
Oxidative Addition

The rate of the oxidative addition of CH_3I to CH_3AuL depends on the nature of L. The rate of addition of CH_3I to $\text{CH}_3\text{AuP}(\text{CH}_3)_3$ is approximately five times faster than the corresponding rate for $\text{CH}_3\text{AuPPh}_3$.⁸ Reaction (2) at high concentrations of CH_3I follows pseudo first order kinetics.⁹ The observed rate constants for eq. (2) were found to be approximately proportional to the CH_3I concentration. A free radical chain process was ruled out by the failure of the free radical scavenger galvinoxyl to affect the rate of the reaction.

The synthesis of dialkylaurate(I)¹⁰ species (eq. 5) provides

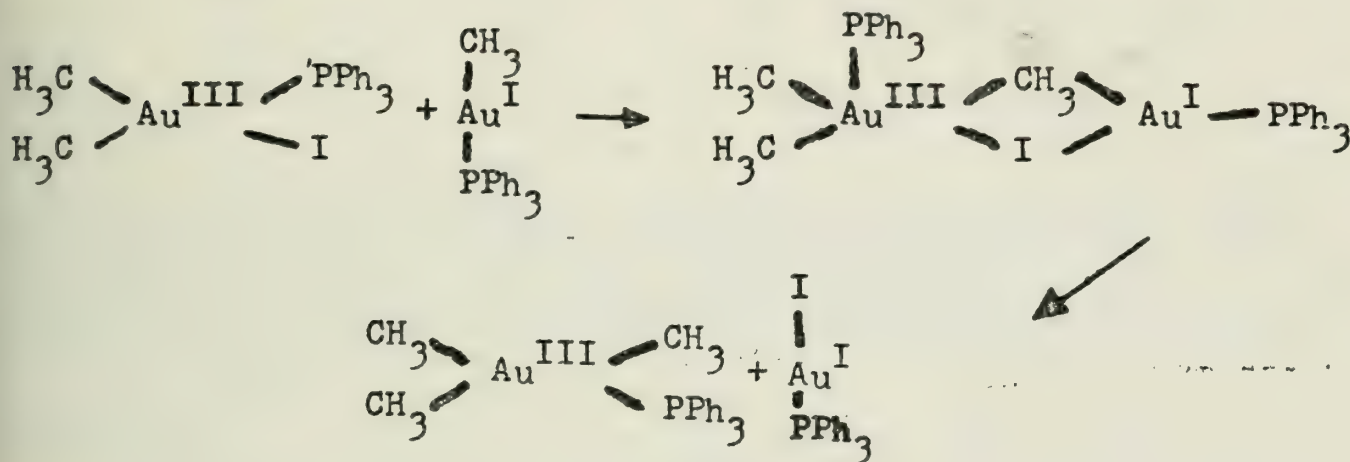


a very reactive anionic organometallate which can oxidatively add alkyl halide instantaneously upon mixing to give trialkylgold species.



Alkyl Exchange

Investigation of the mechanism of the alkylation of dialkyl-gold(III) compounds with alkylgold(I) complexes^{1,1} showed that the mechanism is most likely simple alkyl exchange of the methyl groups.



Alkyl Isomerization

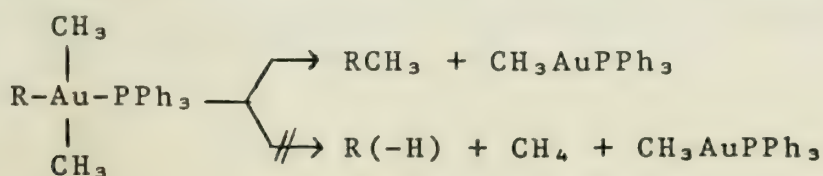
$(\text{CH}_3)_2((\text{CH}_3)_3\text{C-})\text{AuPPh}_3$ was found to isomerize spontaneously to the iso-butyl dimethyl complex in diethyl ether at room temperature.^{1,2} The kinetics of the isomerization were found to be first order in $(\text{CH}_3)_2((\text{CH}_3)_3\text{C-})\text{AuPPh}_3$. The first order rate constant of this reaction was found to decrease with increasing amounts of PPh_3 . An associative mechanism involving the added PPh_3 was ruled out by ^{31}P NMR studies. A dissociative mechanism was proposed to explain the reduction in the rate by added PPh_3 . It appears that the isomerization is primarily due to steric factors since an isopropylgold(III) compound showed no evidence of rearrangement to an n-propyl compound until thermal decomposition occurred. Analysis of the decomposition products indicated the presence of an n-propyl compound.

Cis-Trans Rearrangement

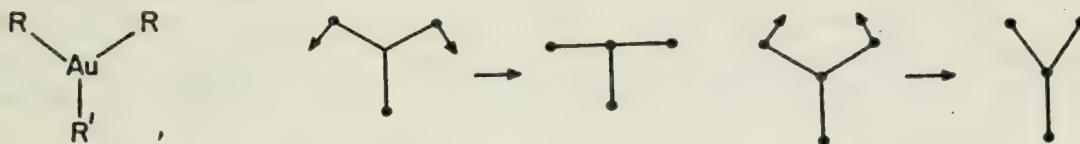
$(\text{R})(\text{CH}_3)_2\text{AuPPh}_3$ compounds were found to favor a trans configuration of the methyl groups. $(\text{CH}_3)_2(\text{CH}_3\text{CH}_2)\text{AuPPh}_3$ formed a mixture of 70% trans, 30% cis at equilibrium. A tetrahedral intermediate similar to that proposed for Ni(II) compounds was suggested.^{1,9}

Reductive Elimination

Reductive elimination from trialkyl gold species results in the coupling of two of the alkyl groups rather than disproportionation.^{1,1} Reductive elimination in nonpolar solvents show



the participation of an intermolecular pathway while polar solvents show exclusively an intramolecular process. The intramolecular pathway can be interpreted by a mechanism that encompasses a three coordinate trialkyl species. Theoretical studies¹⁴ indicate that the most symmetrical (C_{3h}) intermediate is Jahn-Teller active and thus favors a distortion to T and Y shaped intermediates.



The T and Y shaped geometries each show three equivalent energy conformations that are lower in energy than the C_{3h} geometry. The T shaped geometries are the energy minima whereas the Y shaped geometries are saddle points that serve as exit channels for the coupled alkane.

Conclusion

The systematic study of the mechanism of reductive coupling alkyl groups on organogold compounds has lead to some generalizations concerning the processes involved. Oxidative addition of alkyl halides to CH_3Au^IL was found to be dependent upon L. The rate of addition was found to be $L = P(CH_3)_3 > PPh_3$. Reductive elimination is observed through a three coordinate species that by theoretical studies is shown to be distorted from a highly symmetrical intermediate to a energetically more favorable T or Y shape. This distortion allows the appropriate orbitals of the methyl groups to interact forming the carbon-carbon bond of the elimination product.

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F-ORBITAL CHEMISTRY

George M. St. George

November 10, 1977

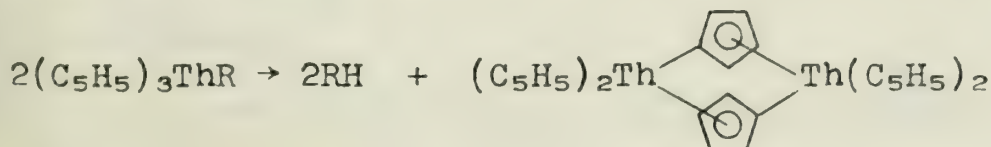
The f-orbitals in lanthanide and actinide elements are of roughly the same energy as the outer s-, p-, and d-orbitals of these elements, and so are energetically available for chemical reactivity. The size and spatial distribution of the f-orbitals can provide the rare-earth elements with a chemistry not found in d-orbital transition metals.

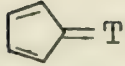
It was originally thought that, while energetically feasible, covalent bonding to rare earths was impossible because of the small radial extension of the f-orbitals and that electrostatics was the dominant theme of lanthanide and actinide chemistry. Early experimental evidence supported this contention: homoleptic rare-earth alkyls, where extensive covalency is expected, were for a long time unsynthesizable; synthesis of halogen-, oxygen-, and nitrogen-donor complexes, on the other hand, were made quite easily; the electronic spectra of these latter complexes were almost identical to those of the free ions--calculation of the nephelauxetic parameter, β , indicates less than 3% covalency in these complexes;^{1,2} and the magnetic properties of these complexes are also very similar to those of the free ions.

More recently, several organo-lanthanide and -actinide compounds have been made. The earliest were $\eta^5\text{-C}_5\text{H}_5$ compounds, followed by $\eta^3\text{-C}_5\text{H}_5$, $\eta^3\text{-C}_3\text{H}_5$, and $\eta^6\text{-C}_6\text{H}_6$ compounds. The electronic spectra of lanthanide and actinide tricyclopentadienides indicate minimal covalency (5%) in these compounds,³ but still greater than in non-carbon-donor compounds. $^1\text{H-nmr}$ studies of $\text{U}(\text{C}_5\text{H}_5)_4$,^{4,5} $\text{Th}(\text{C}_5\text{H}_5)_4$,⁵ and $\text{U}(\eta^3\text{-C}_3\text{H}_5)_4$ ⁶ indicate that dipolar contributions are most important in the isotropic proton shifts, indicating little covalency in these complexes. $^1\text{H-nmr}$ studies of cyclooctatetraenyl compounds, however, indicate not only strong covalent interactions but also that these interactions are ligand π to metal-f charge transfer in character.⁷

Early attempts at synthesis of homoleptic alkyl complexes led to pyrophoric, uncharacterized complexes. By blocking off most of the metal coordination spheres with cyclopentadienyl rings, compounds of the form $(\text{C}_5\text{H}_5)_n\text{MR}$ were made;^{8,9,10,11} these compounds have high thermal stability, though they are highly sensitive to oxygen and moisture. Nmr studies indicate high covalency in the M-R bond. In lanthanide complexes of this type, a ligand-to-metal charge transfer band is seen in the near UV; hypersensitivity is seen in the f-f transitions of certain compounds of this type, indicating covalency in the bonding.¹¹

The decomposition of $(\text{C}_5\text{H}_5)_3\text{ThR}$ has been studied in detail;⁹ decomposition occurs by intramolecular abstraction of a proton from a C_5H_5 ring by the alkyl group.



A "carbene" intermediate, , has been proposed for this reaction. Although no stable carbene complex of a rare-earth element has been synthesized, a recent angular-overlap-model study has demonstrated the possibility of π -bonding in this manner by f-orbitals.¹²

With the exception of $(\phi_4\text{La})^-$ and $(\phi_4\text{Pr})^-$, homoleptic rare-earth alkyl complexes were uncharacterized until quite recently. In situ reaction of UCl_4 with four equivalents of RLi led to alkane and alkene thermolysis products via a proposed UR_4 intermediate.¹³ Recent evidence indicates that the intermediate may be of the form $(\text{UR}_6)^=$, as isolable compounds of this type have been synthesized, as have $(\text{UR}_6)^{3-}$ complexes.¹⁴ The octaalkyluranate(V) complexes have remarkable thermal stability and appear to be coordinatively saturated.

As well as the recent appearance of new and interesting lanthanide and actinide complexes,^{9,11,15} there has been great interest in finding new uses for longer-known complexes utilizing the peculiar coordination geometries of f-orbital elements.

While the rare earths have been a subject of study for many years, it was not until the late 1960's and the discovery of isolable organo-metallic complexes of these elements that intensive study was undertaken; and much remains to be learned about these elements and their compounds. Indications of covalency in these complexes supports the importance of the f-orbitals (as opposed to other effects) in the unique chemistry of rare-earth complexes. There is great promise of exciting discoveries, both theoretical and synthetic, in this field.

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THEORY AND APPLICATIONS OF EXTENDED X-RAY ABSORPTION FINE STRUCTURE ANALYSIS (EXAFS)

Paul Young

November 17, 1977

In recent years, analysis of the irregular oscillations in the atomic x-ray absorption coefficient (EXAFS) has provided valuable structural information on systems where conventional x-ray diffraction methods are inapplicable. Since EXAFS can be observed for gasses, solutions, and amorphous solids, exciting advances have been made involving these forms of matter.

Although EXAFS has been known since the 1920's,¹ no satisfactory and useful theory was presented until 1971.² Present theories, which are used to obtain interatomic distances, explain EXAFS as a backscattering interference effect on the final state in the photoelectric absorption process. For the purposes of EXAFS, the ejected photoelectron can be considered as an expanding spherical wave of wave vector k , $k = \sqrt{2(\Omega - E_0)}$, where Ω is the x-ray energy and E_0 is the threshold energy.³ This final state will be scattered and phase shifted by the neighbors, and the backscattered wave will constructively or destructively interfere with itself at the absorbing atom, thus enhancing or reducing the absorption probability.⁴ Since the backscattering factor, f , and the phase shift, η , are functions of k , the final effect on the absorption coefficient, $\chi(k)$, is not simple.⁵ Because the phase shift and wave vector are not known, problems of interpretation have plagued investigators.⁶ Several methods have been published to determine η and E_0 ,^{6,7,8} but in practice, model compounds of known structure are used to empirically determine atom-pair phase shifts and to guide judicious truncation of data to minimize the effect of choice of E_0 . The Fourier transform of the data is then obtained, giving the radial distribution of scatterers.^{9,10} Least squares fitting of the EXAFS parameters to the data has also been accomplished.¹¹

Experimentally, EXAFS has experienced a renaissance with the completion of the high intensity x-ray source at the Stanford Linear Accelerator Center.¹² This beam is 10^5 times brighter than conventional x-ray tubes, and provides a continuous spectrum from 4000Å down to 0.3Å. A crystal monochromator is used to select energy and obtain the EXAFS spectrum.

Many systems have been investigated with EXAFS. The first Fourier transform studies of the EXAFS method compared the known structure of crystalline germanium with that of amorphous germanium and found smearing due to distortion of bond angles.^{2a} In a more recent example, the coordination of copper in the semiconductor $\text{Cu}_x(\text{As}_{0.4}\text{Se}_{0.6})_{1-x}$ has been shown to be quite similar to that in crystalline CuAsSe_2 .¹³

EXAFS is a useful tool for study of bioinorganic molecules as well. The detection of four equivalent Fe-S bonds in rubredoxin¹⁴ and of three sulfur atoms to molybdenum¹⁵ in nitrogenase are impressive examples. An EXAFS spectrum has even been taken of in vivo manganese of a leaf.¹⁶ The coordination spheres of iron(III) and nickel(II) in aqueous solution have been determined, and hydroxide bridged dimers of iron(III) have been found.^{17,18} Finally, EXAFS of highly dispersed supported metal particles and the combination of EXAFS and Auger techniques have probed the structure of surfaces. One example is the discovery that dioxygen coordinates to a Cu-Ru catalyst at a Ru₃ group with the same Ru-O distance as in RuO₂.¹⁹

In summary, EXAFS, which is dependent on backscattering by the local environment of the absorbing atom, is one of the most powerful and exciting structural techniques in many years. Detailed studies of previously unknown structures have advanced markedly, and further advances will tantalize chemists for years to come.

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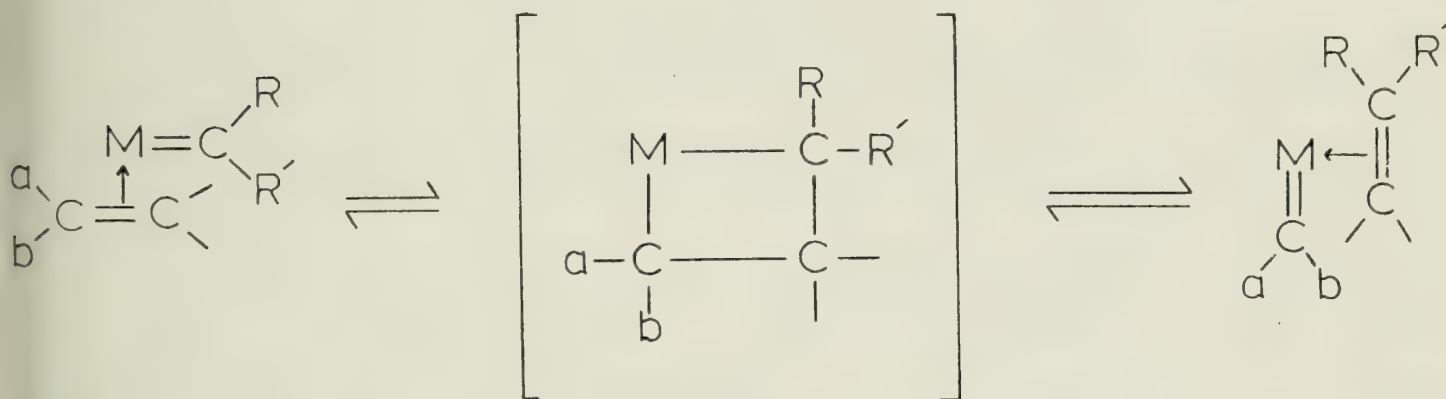
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MECHANISTIC STUDIES OF THE OLEFIN METATHESIS REACTION

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Within three years of the first reported catalytic metathesis of olefins (1964) the process had become industrially significant.¹ A wide variety of homogeneous and heterogeneous catalysts have been reported to catalyze the metathesis of an equally diverse set of olefin types. Following the discovery that the olefin double bonds were broken during the course of the reaction,² several mechanisms appeared which shared the common feature of "pairwise" transalkylidenation. The transition state was hypothesized to be "quasicyclobutane" or "tetramethylene" metal complexes or a metallo-cyclopentane. More recent studies suggest that the reaction proceeds via a metal carbene-initiated chain process. The first mechanistic scheme implicating metal carbenes was proposed in 1970 by Chauvin and Herrisson to explain the formation of high molecular weight polyalkenamers at low conversions during the metathesis of cycloolefins.³ Very recently, model studies have been conducted which support the formation of a puckered metallo-cyclobutane as the key step in the metathesis of olefins.⁴ A mechanistic scheme incorporating these features has become generally accepted and is presented below.



The formation of high molecular weight polyalkenamers as "first-formed" products of the metathesis of cycloolefins⁵ and the presence of sesqui-oligomers⁶ suggested that a chain mechanism was operating in the catalyst systems studied. However, only the cross metathesis of acyclic and cycloolefins⁷ and the metathesis of isotopically labelled α, ω -dienes⁸ provided unequivocal evidence that the chain mechanism was operating in these systems. Support for the metal carbene mechanism has come recently also from quenching experiments with Michael acceptors,¹⁰ from systems containing electron-rich olefins in which metal carbenes can be isolated under metathesis conditions,¹¹ and from numerous model studies. The isolation of non-heteroatom stabilized metal carbenes, first reported by Casey^{12a} and by Schrock,^{12b} initiated a large number of modelling experiments. In at least one case, a metal

carbene has been shown to be an active catalyst for olefin metathesis.¹³

In an elegantly designed labelling study Grubbs has elucidated the mode of initiation for two different homogeneous catalyst systems.⁹ A parallel between metathesis activity and extent of formation of active catalyst in the initiation step was shown and the suggested dimerization of metal-methylene species would provide a chain termination mechanism.

Because of the range of catalysts for the olefin metathesis reaction and the variety of olefin types studied, it is entirely possible that no single mechanistic scheme will prove general. However, the suggestion that the olefin metathesis reaction is initiated by a metal carbene complex and proceeds through a metallocyclobutane intermediate allows rationalization of all the presently available data, including the details of selectivity during metathesis.^{14,15}

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EXPERIMENTAL APPLICATIONS OF THE ANGULAR OVERLAP MODEL

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The spectral and magnetic properties of transition metal complexes can to a large extent be explained in terms of the d electron configurations of the metal. Crystal field, ligand field, and molecular orbital calculations have all been used to explain these properties. Methods have been developed which try to combine the principles of semi-empirical molecular orbital calculations with chemical intuition. An approach of this type is the angular overlap model (AOM),¹⁻⁵ the name being derived from the fact that the squares of the overlap integrals between the metal d orbitals and the appropriate ligand orbitals are proportional to the destabilization energy of the d orbitals in the complex.

The AOM parameters can be used to describe the energies of the d orbitals in terms of σ , π , and δ interactions. The parameters arise from a perturbation theory treatment coupled with the Wolfsberg-Helmholz approximation.⁶ This allows the destabilization energy of a d orbital to be written as

$$E^* = \left(\frac{H_L^2}{H_M - H_L} \right) S_{ML}^2$$

where H_L and H_M are the coulomb integrals for the ligand and the metal, and S_{ML} is the overlap integral. By factoring S_{ML} into radial (S_{ML}^*) and angular (F_λ^ℓ) parts, the energy is now written as

$$\begin{aligned} E^* &= \left(\frac{H_L^2}{H_M - H_L} \right) (S_{ML}^*)^2 (F_\lambda^\ell)^2 \\ &= e_\lambda (F_\lambda^\ell)^2 \end{aligned}$$

where e_λ is defined as the AOM radial parameter with $\lambda = \sigma, \pi, \delta$ for each type of orbital interaction. F_λ^ℓ , with ℓ denoting the azimuthal quantum number, is the angular overlap integral and is obtained from matrices derived for p, d, and f orbitals.^{7,8} For a metal complex with N ligands, it is assumed that the contributions from each ligand are additive giving

$$E^* = e_\lambda \sum_{k=1}^N (F_\lambda^\ell)^2$$

The total angular overlap effect is found by summing the F_λ^ℓ values obtained for each ligand having coordinates (θ_k, ϕ_k) . Consequently, each d^* level can be described using a combination of angular coefficients and radial parameters of the form $Ae_\sigma + Be_\pi + Ce_\delta$.

The AOM has been applied to a wide variety of chemical systems and has yielded many types of chemical correlations.

A series of trans-tetraamine and trans-tetrakis (pyridine) chromium(III) complexes has been examined using the AOM.⁹ Solution absorption spectra and a transferability assumption for parameters were used to construct a two-dimensional spectrochemical series of ligands for chromium(III). The π parameter for the chromium(III) to pyridine bond was found to be negative, indicating the presence of π -back bonding. The single crystal linearly polarized electronic spectra of tetragonal $\text{Ni(en)}_2\text{-(NCS)}_2$ and $\text{Ni(en)}_2\text{(NO}_2\text{)}_2$ were used to derive e_σ and e_π parameters.¹⁰ These were used along with other nickel amine AOM values to determine a linear relationship between e_σ and nickel-nitrogen distance. Correlations of this type are valuable in interpreting other systems as evidenced by Purcell's study of the isomers $\text{Fe(phen)}_2\text{(NCBH}_3\text{)}_2$ and $\text{Fe(phen)}_2\text{(CNBH}_3\text{)}_2$.¹¹ Apparent discrepancies among the IR, magnetic, and Mossbauer data were explained using AOM correlations.

The AOM has also found use as a means for determining the relative energies of the d orbitals in a number of copper(II) complexes.¹²⁻¹⁵ A study of some copper(II) acetylacetonate complexes has verified the orbital energy sequence suggested by Belford.¹⁶ Likewise, the energies of the electronic states of Co(salen) , Co(salen)dimer , and Co(salen)py have been calculated¹⁷ using the AOM and they satisfactorily account for the observed electronic and EPR spectra. Gerloch has obtained the same type of success using the AOM to parameterize his ligand field method for calculating optical and EPR spectra and magnetic susceptibilities.¹⁸⁻²⁰

The angular overlap model is beginning to have widespread application in the correlation and rationalization of experimental results on transition metal systems. Due to the chemical significance of its parameters, the AOM should continue to gain popularity among inorganic chemists.

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CHEMISTRY OF THE EXCITED STATE OF
TRIS(2,2'-BIPYRIDINE)RUTHENIUM(II)

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Since the first reported use¹ of tris(2,2'-bipyridine)-ruthenium(II), $\text{Ru}(\text{bipy})_3^{2+}$, as a photosensitizer in the aquation of PtCl_4^{2-} , a great deal of work has been done on the luminescent quenching of $\text{Ru}(\text{bipy})_3^{2+}$. Several features² of $\text{Ru}(\text{bipy})_3^{2+}$ make it especially attractive for study; these include water solubility, strong visible absorption ($\epsilon \sim 14000$ at 450 nm), photostability, a low-lying (17.8 kK) excited state, and strong luminescence with a lifetime of approximately 0.7 microseconds in aqueous solutions at room temperature.

Although the exact nature of the reactive excited state has not been completely resolved, studies indicate that it is a manifold of three thermally equilibrated metal-ligand charge transfer states of A_1 , E , and A_2 symmetry.³ There is general agreement that the emitting state is predominately triplet in character, although the large amount of spin-orbit coupling present makes difficult an exact assignment to the spin multiplicity.

Energy transfer is one important mechanism⁴ for quenching in $\text{Ru}(\text{bipy})_3^{2+}$. Two studies that illustrate unambiguous energy transfer in fluid media involve quenching by $\text{Cr}(\text{CN})_6^{3-}$ ⁵ and by a series of organic compounds⁶ known to be efficient triplet energy acceptors.

Since there is considerable charge separation in the luminescent excited state,⁷ $\text{Ru}(\text{bipy})_3^{2+}$ should have both oxidizing and reducing sites and electron transfer quenching, both oxidative and reductive, could be expected. Oxidative quenching of $\text{Ru}(\text{bipy})_3^{2+}$ has been extensively studied, but direct observation of the electron transfer products is made difficult by the fact that the $\text{Ru}(\text{bipy})_3^{3+}$ formed in the quenching process is a strong oxidizing agent.⁷ As a result, the initial quenching reaction is followed by a rapid dark thermal reaction to regenerate $\text{Ru}(\text{bipy})_3^{2+}$ and the oxidized form of the quencher.⁸ The mechanism of the quenching by $\text{Co}(\text{NH}_3)_5\text{X}$ ($\text{X}=\text{NH}_3, \text{H}_2\text{O}, \text{Cl}^-, \text{Br}^-$) resulting in the redox decomposition of the $\text{Co}(\text{III})$ complex has been the subject of some controversy,⁹⁻¹¹ but electron transfer is presently favored.¹² Flash photolysis¹³ and steady state¹⁴ studies of quenching by $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ indicate that this species also quenches by an electron transfer mechanism. Oxidative quenching of $\text{Ru}(\text{bipy})_3^{2+}$ has been observed for various organic quenchers. As the reduction potentials of members of a series of nitrobenzene derivatives are varied from -0.525 V to -1.203 V, the observed quenching rate constant decreases by four orders of magnitude.¹⁵ Two other organic quenchers which cause oxidative quenching are 1,1'-dimethyl-4,4'-bipyridine (paraquat, P^{2+}) and trans-1,2-bis(N-methyl-4-pyridyl)ethylene (trans-4,4'-BPE).¹³ That electron transfer quenching is observed for trans-4,4'-BPE is significant because this quencher has a low-lying triplet state that should be readily accessible to $\text{Ru}(\text{bipy})_3^{2+}$ for energy transfer quenching.

The first suggestion that reductive quenching of $\text{Ru}(\text{bipy})_3^{2+}$ occurs was made by Creutz and Sutin¹⁶ who observed that $\text{Ru}(\text{NH}_3)_6^{2+}$, $\text{S}_2\text{O}_4^{2-}$, $\text{Fe}(\text{CN})_6^{4-}$, and $\text{Eu}(\text{III})$ quenched the $\text{Ru}(\text{bipy})_3^{2+}$ luminescence with rates very similar to the rates at which these species were known to reduce horse heart ferricytochrome c. Balzani and co-workers¹⁷ found evidence for the formation of $\text{Mo}(\text{CN})_8^{3-}$ and $\text{Os}(\text{CN})_6^{3-}$ when $\text{Mo}(\text{CN})_8^{4-}$ and $\text{Os}(\text{CN})_6^{4-}$, respectively, were used as quenchers. Further evidence for reductive quenching comes from studies using organic quenchers. When N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) and 10-methylphenothiazine (10-MPTH) were used as quenchers, spectral evidence for formation of TMPD^+ and 10-MPTH^+ was obtained.¹⁸ The absorption spectrum of $\text{Ru}(\text{bipy})_3^+$ calculated from flash photolysis studies of the TMPD system agreed well with that obtained from electrochemically generated $\text{Ru}(\text{bipy})_3^+$.

The observed photochemistry of $\text{Ru}(\text{bipy})_3^{2+}$ suggests several applications in converting light energy to more useful forms. In a study using paraquat (P^{2+}) as a quencher in the presence of triphenylamine, $\text{Ru}(\text{bipy})_3^{2+}$ has been observed to drive the reaction $\text{P}^{2+} + \text{NPh}_3 \rightarrow \text{P}^+ + \text{NPh}_3^+$ in the nonspontaneous direction with conversion of 69% of the excited state energy of $\text{Ru}(\text{bipy})_3^{2+}$ into the chemical energy of the P^{2+} - NPh_3 system.¹⁹ Sutin has constructed a photogalvanic cell, in which the $\text{Ru}(\text{bipy})_3^{2+}$ - $\text{Fe}(\text{III})$ system is observed to generate a potential upon irradiation of half of the cell with light of a wavelength appropriate to produce $\text{Ru}(\text{bipy})_3^{2+*}$.²⁰ Sutin has suggested a design for a cell containing only $\text{Ru}(\text{bipy})_3^{2+}$ in basic solution with an n-type semiconducting electrode and a Pt electrode that should theoretically be able to reduce water to H_2 and O_2 .²¹ However, construction of a working model has not been reported to date. Whitten's report²² of surfactant derivatives of $\text{Ru}(\text{bipy})_3^{2+}$ causing decomposition of water was later found to be irreproducible²³ upon rigorous purification of the surfactants; it was suggested that some impurity was the reactive species, but attempts to identify that species have so far been unsuccessful.

These studies have shown that the chemistry of excited state $\text{Ru}(\text{bipy})_3^{2+}$ is quite complex. Perhaps by judicious substitution on the bipyridyl ligand,¹⁴ one could control emission lifetimes and reduction potentials of $\text{Ru}(\text{bipy})_3^{2+}$ compounds, making possible the design of $\text{Ru}(\text{bipy})_3^{2+}$ compounds that will exhibit desirable excited state properties.

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THE PARTIAL MÖSSBAUER PARAMETER AND THE TRANS INFLUENCE IN LINEAR GOLD(I) COMPOUNDS

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The Mössbauer effect¹ has been observed for over thirty isotopes. The Mössbauer observables are the center shift (C.S.) which results from the variation in nuclear electron density and the quadrupole splitting which results from the electric field gradient at the nucleus. For low spin Fe(II) and for Sn(IV) systems, which have no contribution to the field gradient from asymmetric valence electron distribution, ligand contributions to the spectra have been successfully quantified through use of the additivity model.^{2,3} The resulting ligand partial quadrupole splitting (p.q.s.) and partial center shift (p.c.s.) values have been used to give an indication of the modes of bonding and elucidate the structures of various compounds. A study of methyl tin iodides,⁴ however, exposed the shortcomings of the electrostatic model for the additivity of ligand effects. The results were interpreted on the basis of the p-orbital imbalance involved in the bonding of methyl groups and iodide ligands. Furthermore, the additivity model does not successfully include π bonding effects and significant deviations from predicted quadrupole splitting values have been observed for Fe(II) compounds containing strong π acceptor ligands.⁵

Recent Mössbauer investigations^{6,7} of $^{197}\text{Au(I)}$ (d^{10}) compounds have applied the additivity model in attempts to quantify ligand effects without success. Earlier studies on octahedral $^{193}\text{Ir(III)}$ compounds⁸ resulted in p.c.s. and p.q.s. values of little predictive use. For example, bis phosphine compounds had significantly higher C.S. values when the phosphines were cis than when trans. The spectra of Au(I) complexes were used to distinguish geometries;^{6,7,9} however, the p.c.s. and p.q.s. values of ligands calculated for the linear structures could not predict the spectra of other linear compounds not in the original correlation. The ligand orderings of p.q.s. obtained from LAuCl were different than those obtained from $[\text{AuL}_2]^+$. π -bonding was shown not to be important for Au(I) complexes, so lack of predictability results from breakdown of the basic assumption of the additivity model.¹⁰ It is believed that the gold atom concentrates more 6s character into the bonds with strong donors. It is also claimed that a particular ligand's donor strength depends on the other ligands bonded to the central atom.

The effects described above have been offered as an explanation of the trans influence¹¹ and in compounds of higher coordination (e.g., Ir(III) octahedral complexes) an additional cis influence exists. The trans influence, which is an ordering of the ability of a ligand to weaken the bond of the group opposite it in the equilibrium state of a molecule,¹² has been studied by many physical methods.¹³ The ligand orders vary according to the method used, partly due to the limitations of using bond lengths, stretching frequencies or NMR coupling constants as an indication of bond strength. A major problem arises in that most of the complexes used to study the trans influence contain cis ligands which introduces a cis influence, whose effect in both direction and magnitude on the bond studied is not well understood.^{11,14,15}

A recent study¹⁶ of this effect using ^{35}Cl nuclear quadrupole resonance (NQR) spectroscopy on compounds of the formulation LAuCl has the advantage of the absence of the cis influence. The ^{35}Cl resonance is very sensitive to the trans ligand, L, and the NQR results could be correlated with the ^{197}Au Mössbauer data. The temperature dependence of the NQR, which reflects π bonding,^{17,18} indicated increasing Cl^- π donation to gold as the L group became a better π acceptor. The trans influence order, derived from the ^{35}Cl resonant frequency¹⁹ extrapolated to 0°K was: $\text{PET}_3 > \text{P}(\text{C}_6\text{H}_{11})_3 > \text{P}(\text{OME})_3 > \text{PPh}_3 > \text{P}(\text{OPh})_3 > \text{AsPh}_3 > \text{p-MeOC}_6\text{H}_4\text{NC} > \text{PhNC} > \text{SMe}_2 > \text{C}_6\text{H}_{11}\text{NC} > \text{PCl}_3 > \text{PPh}_3\text{S} > \text{py} > \text{Cl}^-$.¹⁶

The combined ^{197}Au Mössbauer and ^{35}Cl NQR results confirm the existence of delocalized bonding effects in linear Au(I) compounds. The importance of π bonding in these compounds is not resolved as the Mössbauer and NQR data do not give similar results. The conclusions do indicate that the additivity model can not be applied to systems where the trans influence is an important consideration.

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POLYMER BOUND SCHIFF BASE COMPLEXES

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Two types of base containing polymers were prepared to investigate the question of site separation^{1,2,3} in coordinate polymer complexes. Co(II) and Cu(II), four coordinate complexes, were incorporated into pyridine and imidazole containing resins through axial coordination to the base residues. The ability of the pyridine polymer to coordinate the Co(II) and Cu(II) species was examined and found to be limited whereas the imidazole polymer binds these species very strongly. Co(DPGB)₂·2MeOH was incorporated into the imidazole polymer and the extent of coordination by the base residues examined by ESR. This Co(II) complex is axial and contains one electron in the d_{z^2} orbital. Axial coordination of one or two nitrogen bases can be distinguished by ESR.⁴ Incorporation of this cobalt complex yielded characteristic 1:1 and 2:1 imidazole-cobalt adducts depending on the loading of the imidazole. The implication for these types of polymers and complexes is that the loading is more important in achieving site separation than is crosslinking.

In addition to the monodentate chelate polymers, the synthesis and characterization of novel multidentate chelating polymers was attempted. Polymer bound complexes based on the H₂SalDPT, H₂SalDAP, H₂SalDAPP and PicDPT ligand systems were prepared through chelation of Mn(II), Fe(III), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II). The ability of the cobalt complexes to reversibly bind O₂ was verified by ESR. The analogous parent complexes were prepared by published procedures^{5,6} as an aid in identification. The heretofore unreported complex Fe(SalMeDPT) was also prepared and characterized by Mössbauer analysis.

The polymer complex (P)-Co(SalDPT) was used in catalytic oxidations of substituted phenols. Both macroreticular and microreticular resin catalysts were employed. In general, the oxidations with the polymer catalyst were slower than those with the parent complex. However, a great enhancement in product selectivity over the parent complex could be achieved with only small changes in the resin loading of the catalyst. The possible effects the polymer is exerting on the catalytic action of the polymer bound complex, to cause such product selectivities, is discussed in terms of what is known about phenol oxidations by cobalt oxygen carriers.^{7,8}

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TEMPERATURE PROGRAMMED DESORPTION AS A TOOL IN CATALYSIS

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Although reactions occurring in solution are routinely investigated by chemists, it is often difficult to get detailed information about reactions which occur on surfaces. Because of the importance of heterogeneous catalysts in industrial processes, however, there is a great deal of interest in heterogeneous surface chemistry. The first step toward understanding these reactions is to learn how reactants interact with the surface. A relatively simple technique for studying the interaction of molecules with a surface is temperature programmed desorption, (TPD).

In TPD, a gaseous reactant is allowed to adsorb on the surface of a catalyst. Physically adsorbed gas is removed and the rate of desorption of chemisorbed gas is measured as a function of temperature. The desorbed gas is typically measured by a thermal conductivity detector.¹⁻³ Alternatively, the desorbed gas may be monitored by a mass spectrometer.^{4,5} The output of a TPD experiment is called a desorption chromatogram,¹ which is a plot of recorder response versus temperature. The recorder response is proportional to the concentration of desorbed gas and the rate of desorption. Desorption chromatograms can provide information about the number of sites which chemisorb a given reactant, and the relative population of these sites. They can also give information about the strength of surface-adsorbate interactions. Finally, under favorable conditions they can provide information about which chemisorption sites are catalytically active.

The type of information which is available from TPD, can be illustrated by results obtained from the ethylene-alumina system. TPD of ethylene chemisorbed on γ -alumina yields two peaks corresponding to two active chemisorption sites.^{6,7} It is found that reaction with hydrogen gas at temperatures below 60°C leads eventually to the hydrogenation of all the ethylene adsorbed on site I.⁷ This indicates that site I, which comprises less than 1.6% of the surface of alumina is responsible for the low temperature hydrogenation of ethylene.

In order to put the interpretation of desorption chromatograms on a more quantitative level, one would like a means of relating T_m , the temperature corresponding to a peak maximum, to the strength of a surface-adsorbate interaction. For the simplest case, where there is first order desorption from an energetically homogeneous surface, and where no readsorption takes place, the following functional equation is used to obtain the activation energy of desorption.¹

$$2\log T_m - \log \beta = E_d/2.303RT_m + \log(E_d/AR)$$

In this equation β is the heating rate, E_d is the activation energy of desorption and A is the Arrhenius constant. If one plots $2\log T_m - \log \beta$ vs. $1/T_m$ for a wide range of β a straight line is obtained, from which E_d and A can be determined. Interpretation of TPD chromatograms can be complicated by readsorption,¹ diffusion from porous surfaces,¹ heterogeneous surfaces,⁸ and second order desorption.^{9,10} Theoretical treatment of these problems have been made, and are included in the above references.

A detailed example of the use of TPD is given by a series of Pt catalysts. Pt is an active hydrogenation catalyst. For this reason a knowledge of how ethylene and hydrogen interact with platinum is desirable. Four forms of chemisorbed hydrogen are obtained from TPD of hydrogen adsorbed on Pt black.¹¹ A fifth hydrogen peak has been observed by other workers, however this data may be suspect.¹²

Ethylene is irreversibly adsorbed on Pt/silica and Pt black. TPD leads only to self-hydrogenation and decomposition.^{13,5} The activation energies of self-hydrogenation and decomposition are 11.1 and 37.3 Kcal/mole respectively. If hydrogen is chemisorbed on Pt, and allowed to react with ethylene, it is found that only the γ , and possibly the β forms of chemisorbed hydrogen participate in the hydrogenation of ethylene.¹⁴

It is interesting that by alloying Pt with Sn one obtains two ethylene desorption peaks, and that the self-hydrogenation and decomposition reactions do not occur.⁵ This is attributed to a dilution of Pt atoms by Sn. This dilution is called an "ensemble effect."¹⁵ The intensity of the high temperature peak decreases at increasing Sn concentrations. This is also attributed to the "ensemble effect." In addition, increasing the concentration of Sn leads to a decrease in the temperature corresponding to the peak maximum. This is attributed to a "ligand effect."¹⁵

In summary, TPD is a simple technique which can provide a great deal of information about practical catalysts. New and improved theoretical treatments as well as improvements in the apparatus itself should lead to greater applicability to the study of metal catalysts. Furthermore, coupling of TPD with TGA, DTA, IR, and other techniques should lead to a better understanding of reactions on the surface of catalysts.

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THE MIXED VALENCE CHEMISTRY OF SOME DISCRETE POLYNUCLEAR IRON AND RUTHENIUM COMPOUNDS

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INTRODUCTION

Mixed valence chemistry is concerned with compounds containing two different formal oxidation states of the same element. Many naturally occurring minerals are mixed valence compounds. Because of their unique characteristics, mixed valence compounds attracted early attention. Mixed valence compounds generally exhibit an intense visible/nir transition arising from the intervalence transfer of an electron. It is this absorption band which gives many mixed valence compounds their characteristic dark coloration. This absorption is attributed to the transition $(2,3) \rightarrow (3,2)^*$, i.e., the Frank-Condon barrier to electron transfer required for a transition between two centers with the same chemical composition but differing in environment due to their different charges.

By 1922, the basic phenomenon of valence oscillation in mixed valence species had been elucidated.¹ Mixed valence chemistry permeates many areas of current interest and many relatively new physical techniques, such as Mössbauer, are being used to study mixed valence enzymes, mixed valence reaction intermediates, and electron transfer in mixed valence compounds.

In 1967, Robin and Day² set forth a classification scheme for mixed valence compounds on the basis of ground state delocalization of the odd electron. Day's scheme contains three classes of mixed valence compounds: those which have no delocalization in the ground state, class 1; those with some delocalization in the ground state or class 2; and, class 3 compounds which experience maximal delocalization of the odd electron in the ground state. Thus, electron exchange between two atoms of different valences can vary from very fast to extremely slow. The properties of these compounds have been found to vary with the extent of delocalization. Class 1 compounds have two atoms in different valence states which do not interact. No intervalence transfer (IT) band is seen. Class 3 compounds, because of the delocalization of the electron, exhibit transitions from a delocalized bonding molecular orbital to an antibonding molecular orbital in the excited state. There is no thermal barrier to electron transfer in the ground state of a class 3 compound.

N. S. Hush has advanced a theory³ to explain the properties of class 2 compounds. The energy of the IT band is used to calculate the rate of thermal electron transfer and the IT band intensity is used to evaluate the extent of ground state delocalization.

RUTHENIUM COMPOUNDS

Many physical techniques have been applied to mixed valence ruthenium dimers to study their electronic exchange. In the case of bis(pentaammineruthenium) pyrazine,⁴ such varied techniques as optical spectroscopy,⁴ Mössbauer,⁵ NMR,⁶ EPR,⁶ IR,⁷ and X-ray crystallography⁸ have been used to determine the rate at which the

electron is exchanging. The application of a battery of physical techniques is common in characterizing a mixed valence system. In determining the rate of thermal electron transfer, the inherent time resolution of the different methods is used. In a series of bis(pentaammineruthenium)L compounds where L is variously pyrazine, 4,4' bipyridyl and cyanogen, Taube and coworkers^{4b,c} reported on the extent of delocalization based on optical spectroscopy where the time resolution is 10^{-13} sec. Only the cyanogen bridged species is delocalized on this time scale. In this compound only one CN stretch is seen at a frequency intermediate between that for the Ru^{+3} and the Ru^{+2} compounds. This indicates that in 10^{-13} sec the cyanogen bridge cannot distinguish between the two ruthenium centers. In the pyrazine and 4,4' bipyridyl bridged compounds, the electron is exchanging slow enough so that bridging ir frequencies show the presence of two distinct ruthenium sites.

IRON COMPOUNDS

Biferrocene derivatives have proved particularly amenable to mixed valence studies. Biferrocene, biferrocenylene and [1.1] ferrocenophane have all been prepared as mixed valence species. These compounds have been studied by polarography,⁹ visible/ir spectroscopy,¹⁰ Mössbauer,¹¹ EPR,¹¹ and magnetic susceptibility.¹¹ Related series of these compounds have been studied and correlations with Hush's theory have been made.¹² The IT band maxima of unsymmetrically substituted biferrocenes are blue shifted from the maxima of symmetrically substituted biferrocenes. This is expected since in unsymmetrically substituted species electron exchange resulting in an unfavorable valence isomer will require more energy.

CONCLUSIONS

There are many mixed valence systems yet to be investigated. The iron-sulfur proteins contain two valence states of iron in polynuclear clusters. Model compounds are being investigated, but the proteins themselves are not as easily studied. Elucidation of the mechanism of electron exchange in these species will enable us to better understand electron transport in biological systems. Also, many mixed valence compounds are being looked at today as possible new semiconductors and even high temperature superconductors because of the enhanced conductivity of many mixed valence compounds.

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"METAL-QUINONE COMPLEXES"

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Introduction

Metal-quinone interactions have been a topic of considerable interest. Quinones are postulated to play important roles in many biological systems. For example, ubiquinones are an integral part of the respiratory electron transport chain, and plastoquinones are involved in photosynthesis.¹ Quinones can act as either one or two electron acceptors. ($Q \xrightleftharpoons{+e^-} SQ^{\cdot-} \xrightleftharpoons{+e^-} HQ^{2-}$.) Due to this interesting redox chemistry, quinones are thought to be "unique" ligands for inorganic complexes. The following are the three general types of metal-quinone interactions: π -type with para-quinones, σ -type with either para-quinones or ortho-quinones and finally donor-acceptor complexes which will not be discussed in this seminar.

Physical Properties

Metal-quinone compounds can be characterized by the following physical techniques: infrared (CO stretch), EPR, NMR, magnetic susceptibility, Mössbauer, electrochemistry and X-ray crystallography. The majority of the inorganic complexes have been identified by the characteristic shift to lower energies of the infrared ν_{CO} band resulting from coordination to a metal. The carbon-oxygen stretching vibrations of ortho-quinones shift 250 cm^{-1} to 300 cm^{-1} . p-Quinones experience shifts of 20 cm^{-1} to 100 cm^{-1} with π -bonding, and shifts of 180 cm^{-1} to 250 cm^{-1} with a σ -type interaction.²

π -Complexes

The π -complexes between para-quinones and metals are formed when the quinones act as "diolefins." The metal bonds with the π electron density of the "ring" rather than direct interaction with the oxygen atoms. The compound (π -duroquinone) iron tricarbonyl is an example of a complex in which the quinone is acting as a $4e^-$ (η^4) donor to the iron.^{3a} Bodner has prepared a η^6 -hydroquinone complex $[(C_{10}H_{12}O_2)M(C_5H_5)]^{+2}$ in solution and characterized it by NMR. The data indicate reduction of the 1,4-benzoquinone moiety has occurred, allowing it to act as a $6e^-$ donor.^{3b} There are no reports in the literature of π -complexes of ortho-quinones.

σ -Complexes

Both ortho-quinones and para-quinones bond to metals in a σ -fashion (i.e., through the oxygen atoms). Numerous σ -complexes of para-quinones have been reported. One of the first to be reported was $K_6[(NC)_5Co(C_6H_4O_2)Co(CN)_5]$. In this complex the dianion form of 1,4-benzohydroquinone is postulated to be bridging between the two pentacyano cobaltate(III) groups.⁴ Calderazzo and coworkers have prepared some Schiff base complexes of cobalt and iron. They are $[Co(salen)(py)]_2C_6H_4O_2$ and $[Fe(salen)]_2$ -quinone where salen = N,N'-ethylenebis(salicylideneiminato).^{5,6} These compounds have been

extensively studied with IR and magnetism. Interesting magnetic properties arise for the cobalt complex [$\mu_{\text{eff}} \approx 0.74$ B.M. at 287K) and the iron complex ($\mu_{\text{eff}} \approx 5.76$ B.M. at 297K). These complexes consist of the dianion of the hydroquinone bridging between two metal(III) centers. In the case of the iron compounds weak anti-ferromagnetic exchange interactions ($-6.1 \geq J \geq -0.19$) are indicated by low temperature susceptibility results.

There are indeed many examples of orthoquinone-metal complexes found in the literature. One finds ortho-quinones coordinated to metals in the three possible forms: neutral quinones, semi-quinones, and hydroquinone dianions. The catechol complex (3,5-di-tert-butylcatecholato) (triethylenetetramine) cobalt(III) chloride is an example of the hydroquinone dianion form.⁷ This complex is characterized by two prominent infrared bands (the C-C skeletal vibration at 1480 cm^{-1} and the carbon-oxygen stretching vibration at 1250 cm^{-1}). Electrochemical studies on the compound indicated a stable "one electron" oxidation product. The isolated species, $[\text{Co}(\text{trien})(\text{DB}_{\text{sq}})]\text{Cl}_2$, was thus formulated with a coordinated semiquinone. The presence of a semiquinone is supported by infrared and EPR data. The carbon-oxygen stretching vibration is at 1440 cm^{-1} . Solution and solid EPR spectra show an eight line hyperfine pattern attributed to ^{59}Co ($I = 7/2$). The cobalt hyperfine coupling constant ($A_{\text{Co}} = 9.67$ gauss) is rather small in comparison to other Co(II) complexes. This indicates the unpaired electron resides in a molecular orbital localized mainly on the semiquinone ligand.⁸

An example of a neutral quinone complex is found in the work of Floriani.⁹ $[\text{TiCl}_4(\text{quinone})]$ was prepared specifically to study the perturbation of a metal interacting with a neutral quinone species (in this case quinone = 9,10 phenanthrenequinone). No shift in the carbon-oxygen stretching vibration was observed in the infrared.⁹

Biological Systems

Ubiquinones are believed to be an important link in the respiratory electron transport chain, playing an essential role in the enzymatic reactions of succinate dehydrogenase. EPR results indicate an interaction between an ubisemiquinone and a second paramagnetic species. Three candidates for this second species have been hypothesized: a second ubisemiquinone, a flavin-semiquinone, and a Fe-S center (namely S_3). Ruzika and coworkers have concluded from their studies that the second species is a flavin-semiquinone.¹⁰ Ohnishi, on the other hand, supports the hypothesis of a Fe-S center (S_3).¹¹ These systems have been studied extensively and are still not completely understood.

Conclusions

The vast area of metal-quinone interactions have been studied for some time, but only the beginnings of this fruitful area have been harvested. This should be an open invitation to inorganic chemists to prepare and characterize inorganic model complexes as an aid to further the understanding of metal-quinone interactions in biological systems.

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ELECTROCHEMICAL REDUCTION OF O_2 ON PHTHALOCYANINE

COMPLEXES

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Because of the need to develop the technology for new energy sources and to improve that of present ones, there is increased interest in fuel cells. As direct converters of chemical to electrical energy, fuel cells are not subject to Carnot cycle limitations. Generally, the oxidant in fuel cells is O_2 , which is attractive because of its availability in air; however, the oxygen electrode is also the major problem in fuel cells because the sluggishness of the electrode reaction $O_2 + 4e^- \rightarrow 2H_2O$ lowers the cell voltage and the power output.^{1,2}

The most widely used electrode materials have been noble metals such as platinum; however, even platinum, one of the best electrocatalysts available for O_2 reduction, performs poorly in comparison to its ability to catalyze other electrochemical reactions. Because of the cost and low world supply of platinum, wide-spread use of fuel cells requires the development of other electrode materials, especially non-metallic ones.² Some of the other materials which have been tested are various oxides of the spinel and perovskite crystal types, tungsten bronzes, disulfides, thiospinels, and various metal chelates, including tetraphenyl porphyrin and phthalocyanine complexes.³ Some of the studies of the activity of phthalocyanine complexes will be examined here.

Various metal chelates of N_4 (tetraaryl porphyrins, dibenzotetraazaannulenes, phthalocyanines), N_2O_2 (polymeric "saloph" complexes), and N_2S_2 [diacetyldi(thiophenylhydrazones)] donor sites have been investigated as electrode materials; only the complexes of N_4 donor sites, all of which are macrocyclic and have extensive π -conjugation, were electrochemically active for the reduction of O_2 . The electrochemical process evidently is not the reduction of a transition metal complex- O_2 adduct formed in solution, as the "saloph" complexes, known to reversibly bind O_2 , were inactive;⁴ also, the diffusion limiting current for reduction of O_2 on Co(II)tetrakisulfonatephthalocyanine adsorbed on graphite was found to be independent of the concentration of complex in solution. As electrode materials, the most active phthalocyanine complexes are polymeric, and contain iron or cobalt;⁶ their activity, which depends greatly on the support, is best on high surface-area carbon.⁷ The activity of these complexes has been tested in acidic, basic, and neutral solutions; while several electrodes containing iron phthalocyanines were found to be unstable in acid,⁴ Meier and coworkers have made electrodes which are stable, at a constant current flow of $20\text{mA}/\text{cm}^2$, for 3000 hours.⁸ Through use of a radioisotopic tracer, Meier monitored the dissolution of iron into 6N H_2SO_4 solution, and

found no direct correlation with the potential drop of the cell with time.⁸ Various correlations between electrocatalytic activity and electrochemical oxidation potentials, magnetic properties, catalytic activity,⁹⁻¹² and conductivity^{11,12} have been offered.

In attempts to learn about the active sites, Mössbauer,^{8,13-15} optical spectroscopy,¹³ and ESCA¹⁵ have been used. Some of the studies have paid insufficient attention to the bulk vs. molecular properties, and the vast effect of ambient conditions (O_2, H_2O) on the conductivity and behavior of the phthalocyanine complexes. (References discussing these effects include 16 and 17).

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SYNTHESIS AND STEREODYNAMICS OF CYCLOPENTADIENYL RHODIUM AND IRIIDIUM CLUSTER COMPLEXES

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Recently it was reported^{1,2} that trimethylamine oxide (Me_3NO) would react with coordinated carbonyls of transition metal complexes producing CO_2 and a coordinately unsaturated complex. This provides a method for inducing relatively quantitative carbonyl loss under mild conditions. Since CO loss in the absence of additional ligands may lead to metal-metal bond formation,³ we have investigated the use of Me_3NO to facilitate cluster formation from coordinately saturated monometallic carbonyl complexes.

The reaction of Me_3NO and $\text{CpRh}(\text{CO})_2$ ($\text{Cp} \equiv \eta^5\text{-cyclopentadienyl}$) produces the known complexes $\text{Cp}_2\text{Rh}_2(\text{CO})_3$, $\text{C}_{3V}\text{-Cp}_3\text{Rh}_3(\text{CO})_3$ and $\text{Cs-Cp}_3\text{Rh}_3(\text{CO})_3$ in much better yields than were obtained by photolysis of $\text{CpRh}(\text{CO})_2$.^{4,5,6} In addition, a previously unknown species, $\text{Rh}_4\text{Cp}_4(\text{CO})_2$, was isolated.

Rhodium-rhodium coupling constants⁷ have been derived from the analysis of high resolution proton NMR spectra of $\text{Cp}_2\text{Rh}_2(\text{CO})_3$, $\text{Cp}_2\text{Rh}_2(\text{NO})_2$ and $\text{Cp}_2\text{Rh}_2(\mu\text{CH}_2)(\text{CO})_2$. The magnitude found for $^1\text{J}_{\text{Rh-Rh}}$, 4-5 Hz, is consistent with that which would be predicted for a simple sigma bond between two rhodium atoms and a coupling mechanism dominated by the Fermi contact term.

The improved syntheses of the C_{3V} and Cs isomers of $\text{Cp}_3\text{Rh}_3(\text{CO})_3$ have made it practical to obtain ^{13}C enriched samples which were necessary for solution characterization. Both isomers are fluxional in solution without isomerization. A novel carbonyl scrambling mechanism has been proposed to explain this behavior.^{8,9} The carbonyls of $\text{Cp}_4\text{Rh}_4(\text{CO})_2$ are also fluxional at ambient temperatures.

Reacting Me_3NO with $\text{CpIr}(\text{CO})_2$ yields $\text{Cp}_2\text{Ir}_2(\text{CO})_3$, $\text{Cp}_3\text{Ir}_3(\text{CO})_3$ and $\text{Cp}_4\text{Ir}_4(\text{CO})_3$. The total yield of isolated species, however, is less than with $\text{CpRh}(\text{CO})_2$.

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POLYMER SUPPORTED HOMOGENEOUS CATALYSTS

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Catalysts are important in many industrial processes, such as petroleum refining, petrochemical manufacture, coal and coal tar derivative processing, and fertilizer manufacture.¹ Generally, catalysts are divided into two categories: heterogeneous and homogeneous. Almost all industrial catalysts are heterogeneous in nature, that is, the reaction takes place at a phase boundary. During the past several years, homogeneous catalysts have received a great deal of attention. These are catalysts which are soluble in the liquid phase reactant. Homogeneous catalysts have received limited industrial use--chiefly because of the difficulty of separation from the reaction products.

Recently, an intermediate system has offered a great deal of promise. Here, the active homogeneous catalyst is firmly held on an insoluble, porous polymeric support. Through such an attachment, it was hoped that the advantages of the homogeneous catalyst would be retained and the disadvantages removed. Many such systems have been studied.²⁻⁶

One type of polymeric support that is commonly used is that of polystyrene-divinylbenzene copolymer resins. By varying the amount of divinylbenzene and hence the crosslinking and pore size in the polymer, one changes the activity and the selectivity of the attached catalyst.

Various functionalized polystyrene copolymers have been employed. Metal complexes have been attached to crosslinked polystyrene by amine,⁷ phosphine, cyclopentadienyl, bipyridyl,⁸ bound imidazole,⁹ and various Schiff bases,^{10,11} among other ligands. The complex is then easily attached by equilibration of the polymeric ligand with a similar or weaker complexing ligand on the metal.

A system of great interest is that of the supported Wilkinson's catalyst, $(PPh_3)_3RhCl$. This complex catalyzes the reduction of olefins by hydrogen at conveniently measurable rates at atmospheric pressure and temperature. While the species attached to a 2% cross-linked resin was found to be about 0.06 times as active as the unsupported catalyst¹² (dependent upon the degree of crosslinking, bead diameter, temperature, and ratio of phosphine to rhodium), it was also shown to be selective toward smaller olefins. Overall activities in the hydrogenation of various types of olefins by the supported catalyst paralleled those reported for the conventional catalyst.¹³ Moreover, the presence of olefin isomerization reactions and significant increases in the selectivity towards the reduction of sterically hindered olefins were observed for the supported catalyst.¹⁴

Grubbs and coworkers¹⁵ have described in detail the selectivity of the supported catalyst on the basis of the olefin size and the polar selectivity. Two opposing factors are considered. As the solvent polarity increases: 1) the pore sizes decrease and 2) a polar gradient is established.

Variable selectivity of this supported catalyst was observed for primary and secondary olefins. This selectivity was found to be dependent on the mode of preparation and the presence of residual nonpolymeric ligands. Comparison was made of the ratio of reduction rate of 1-hexene/cyclohexene for these complexes and those of non-attached species. Using these comparisons, it was shown that the structure of the supported complex is a function of the loading of the metal on the polymer.¹⁶ A more detailed structure of the attached species was obtained using EXAFS.¹⁷

Another system of interest is that of supported titanocene. Titanocene and its hydrides are useful catalysts in the hydrogenation of unsaturated hydrocarbons and molecular nitrogen.^{18,19,20} One of the major problems with this catalyst is it readily dimerizes to form a catalytically inactive species which blocks the open coordination site required for homogeneous catalysis. To prevent this, Grubbs and coworkers²¹⁻²⁴ attached the titanocene precursor Cp_2TiCl_2 to a 20% crosslinked polystyrene-divinylbenzene copolymer resin. Verification that only one species was present on the bead was made using elemental analysis and far infrared studies. The attached species was found to be about twenty times as active a hydrogenation catalyst as the corresponding non-attached species. Pulverized beads showed an increased activity of 8 to 10 times. This was due to the ability of the rigid polymeric matrix to keep the metal centers apart, thus preventing dimerization. This catalyst was also found to be more selective toward the smaller olefins.

The supported titanocene system was tested for its ability to fix nitrogen. In the 20% crosslinked resin, the centers were too far apart for the formation of the theoretical intermediate complex. By lowering the crosslinking, fixation was observed.

Since it was proposed that the increase in activity for the supported titanocene resulted from site isolation on the polymer, site isolation was studied as a function of the loading of the catalyst. This study led to model for site isolation.²⁵

Pittman and coworkers²⁶⁻²⁸ have performed sequential multistep reactions catalyzed by polymer-anchored homogeneous catalysts. The authors compared systems using two different catalysts bound to the same bead and systems with the two catalysts on different beads but mixed together. It was found that such systems could be easily recycled and there was little interference of one catalyst on another. These dual catalyst systems can be employed in one "pot" to perform multistep organic syntheses with intermediate purification steps eliminated.

Although there are several disadvantages to this heterogenizing of homogeneous catalysts, there are many advantages. The major drawbacks are: side reactions resulting in the formation of surface functional groups other than those desired; the increased complexity of the polymeric ligand; and the difficulty in characterizing the active sites. Some of the advantages are: easy separation from the reaction mixture so there is virtually no product contamination by

spent catalyst; reuse without loss of activity; great enhancement in product selectivity; less sensitivity to poisoning impurities; increased activity in some cases; and a great versatility since the polymer support can be easily modified.

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THE BINDING OF DIOXYGEN TO METAL CENTERS

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April 6, 1978

The interaction of molecular oxygen with transition metal compounds has been of interest for a number of years. Recent reviews¹⁻⁵ sum up a large portion of the work that has been reported. Interest in dioxygen compounds has stemmed from their role as oxygen carriers in biological systems (e.g., hemoglobins), and their possible involvement in homogeneous catalysis oxidation processes.

This seminar is concerned with dioxygen binding to transition metals. Dioxygen complexes are known for most transition elements. From a structural viewpoint, these complexes fall into two categories. One consists of end-on binding of O_2 ; the other group is characterized by a sideways-binding of O_2 to the metal. Due to the nature of the metal dioxygen linkage, the end-on complexes are called superoxo O_2^- compounds, while the sideways-bound species are referred to as peroxo O_2^{2-} compounds. Both monomeric 1:1 (i.e., metal: O_2 stoichiometry) and dimeric 2:1 species are known. The connectivity in the 2:1 complexes is of the form M-O-O-M.

A wide range of physical techniques have been employed to investigate structure and bonding in the metal-dioxygen systems. The complexes of both types have been structurally characterized by X-ray analysis.⁶⁻⁷ I.R.-Raman studies^{8,9} have also been helpful in characterizing the complexes, particularly in terms of ν_{O-O} and ν_{M-O} characteristic absorptions. The electronic structure of the complexes have been studied through EPR,^{10,11,12} Vis-UV,¹³ X-ray photoelectron spectroscopy,¹⁴ and Mössbauer spectroscopy.¹⁵ Contradictory interpretations concerning the nature of M- O_2 bond have developed as a result of the spectral studies.

Recent theoretical work by Goddard employing ab initio GVB¹⁶ calculations, by Veillard, using ab initio LCAO-MO-SCF¹⁷ type calculations and also work by Karplus¹⁸ using SCF-CI and X α calculations has shed further light on the nature of the dioxygen-metal interaction.

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SOME ASPECTS OF THE CHEMISTRY OF HYDRIDO BISCYCLOPENTADIENYL METAL COMPOUNDS

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Transition metal hydrides of the general formula Cp_2MH_x undergo a variety of reactions with olefins and acetylenes. The nature of the reaction is determined by the degree of electronic and coordinative saturation of the metal.

Cp_2ZrH_2 readily reacts with electron donating olefins, however, insertion products have never been isolated due to the required reaction conditions.¹ Using Cp_2ZrHCl , a series of stable Zr-alkyl compounds have been obtained.² Once formed, these alkyl compounds will incorporate CO to give the corresponding acyl.³ Reactions of both hydrides with acetylenes have yielded a wide variety of alkenyl complexes.⁴

Cp_2MoH_2 and Cp_2WH_2 are both electron rich and display pronounced basicity.^{5,6,7} A charge transfer interaction is the initial reaction between these hydrides and strong Lewis acids. Continued reaction leads to insertion into the metal-hydrogen bond.^{8,9,10,11,12}

Cp_2NbH_3 and Cp_2TaH_3 are both coordinatively saturated, with all available orbitals used in bonding. Therefore, a mechanism is required which opens the required coordination site. The mechanism demonstrated is the elimination of dihydrogen to produce the reactive intermediates $[\text{Cp}_2\text{NbH}]$ and $[\text{Cp}_2\text{TaH}]$.¹³ These have been found not only to coordinate and react with olefins and acetylenes but also to catalyze the H/D exchange between dihydrogen and benzene.^{13,14,15}

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APPLICATIONS OF PHASE TRANSFER CATALYSIS TO ORGANOMETALLIC
SYSTEMS

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Phase transfer conditions consist of a two-phase system of aqueous base and an immiscible organic solvent.¹ The catalyst, which resides primarily in the aqueous phase, commonly is either a crown ether binding an alkali metal cation or a tetraalkyl ammonium halide salt. Ion pair migration to the organic phase yields very reactive species which may react with the target substrate. This technique was initially utilized in organic chemistry in 1965.² Since that time, the catalysis of organic reactions by phase transfer has exhibited a phenomenal growth. A few examples of reactions facilitated by such means are carbene reactions, nucleophilic substitutions, alkylations of ketones and nitriles, and formation of ethers and esters.³

The first application of phase transfer catalysis to a system containing a transition metal was published in 1973.⁴ Five 1, 1-dichloro-2-ferrocenylcyclopropanes were obtained in high yield by the generation of dichlorocarbene in the presence of the corresponding vinylferrocenes. More recently, several papers have reported organic reactions which are catalyzed or facilitated by metal carbonyls under phase transfer conditions. Formation of ketones or diketones from bromoketones⁵ and synthesis of carboxylic acid derivatives from aromatic halides^{6,7} have occurred in the presence of $\text{Co}_2(\text{CO})_8$. Aromatic nitro compounds may be reduced to the corresponding amines by $\text{Fe}_3(\text{CO})_{12}$.^{8,9} In each of these cases, it is believed that metal carbonyl anions are produced under phase transfer conditions. These anions react with the organic species in the nonaqueous phase to yield the observed products.

Phase transfer catalysis has also been useful in the synthesis of metal complexes. High yield syntheses of cobalt carbonyl compounds derived from $\text{Co}_2(\text{CO})_8$ have been reported.¹⁰ Use of allyl bromide led to π -allylcobalt carbonyls and use of trihalomethyl compounds led to the alkylidynetricobalt nonacarbonyls. By the reaction of thiobenzophenones with $\text{Fe}_3(\text{CO})_{12}$ an interesting ortho-metallated complex may be produced.¹¹ The relatively inert group VI metal carbonyls ($\text{M}(\text{CO})_6$; $\text{M}=\text{Cr}, \text{Mo}, \text{W}$) have been shown to undergo accelerated substitution by tertiary phosphines, triphenylarsine, or dipyridyl in the presence of an aqueous sodium hydroxide/benzene system with tetra-n-butylammonium iodide as the phase transfer catalyst.¹² Neutral group VI and iron complexes have been shown to undergo ^{18}O labeling of the carbonyl ligands under similar conditions when the aqueous layer is H_2^{18}O .¹³ Again, the role of the phase transfer catalyst in each of these reactions apparently is to form a metal carbonyl anion, which then undergoes further reaction.

Phase transfer catalysis has been shown to be applicable for organometallic reaction systems that involve anionic intermediates. In many uses it is preferred to other routes, offering the advantages of optimized yield, reaction time, and other reaction parameters. As this technique is only in its infancy, it will undoubtedly become increasingly important in the future.

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WITH EXTENDED BRIDGING GROUPS

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(Final Seminar)

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Introduction

The study of electron-dynamical phenomena permeates many areas of current chemical research. One of these phenomena, characterized by a weak coupling between the electrons from two or more paramagnetic centers, is known as a magnetic exchange interaction. The strength of this interaction is gauged by the exchange parameter J in the spin Hamiltonian $\underline{H} = -2J \underline{S}_1 \cdot \underline{S}_2$ and this parameter measures the splittings which develop between various coupled electronic states. A variety of materials exhibit exchange interactions, some of which include extended lattice polymers, transition metal clusters in metalloproteins, and organic biradicals. Recent work on di- μ -hydroxo-bridged copper(II) complexes has shown a linear relationship between the exchange parameter and the Cu-O-Cu bridging angle.¹ One objective of the present work has been to establish various criteria for judging the viability of a polyatomic bridging group to support a magnetic exchange interaction between two copper(II) ions. Particular attention has been given to complexes which will elucidate the dependence of the exchange parameter on the copper(II) single-ion ground state and the relative bridge orbitals capable of propagating the exchange interaction.

Oxalate-Bridged Complexes

A series of complexes bridged by the oxalate dianion were prepared having the general formula $[\text{Cu}_2(\text{"dien"})_2(\text{C}_2\text{O}_4)](\text{Y})_2$, where "dien" is dien $[\text{HN}(\text{CH}_2\text{CH}_2\text{NH}_2)_2]$, dpt $[\text{HN}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2]$, Me₅dien $[\text{NCH}_3(\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2)_2]$, or Et₅dien $[\text{NC}_2\text{H}_5(\text{CH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2)_2]$ and Y⁻ is BPh₄⁻, ClO₄⁻, or PF₆⁻. In these complexes the oxalate dianion serves as a relatively inflexible bridging group as the copper(II) geometry changes from square pyramidal (SP) in $[\text{Cu}_2(\text{dien})_2(\text{C}_2\text{O}_4)](\text{ClO}_4)_2$ to trigonal bipyramidal (TBP) in $[\text{Cu}_2(\text{Et}_5\text{dien})_2(\text{C}_2\text{O}_4)](\text{BPh}_4)_2$.^{3,4} Characterization of the complexes with variable-temperature magnetic susceptibility and EPR reveals that the exchange interaction is much greater for the TBP d_z² copper(II) ground state ($J = -37.4 \text{ cm}^{-1}$) than for the SP d_{x²-y²} copper(II) ground state ($|J| \lesssim 0.5 \text{ cm}^{-1}$). The BPh₄⁻ counterion provides a magnetically dilute environment for the binuclear cations and, as such, copper hyperfine splittings appropriate for an exchange-coupled system are observed in the pure solid. The exchange interaction is mediated by the O-C-O portion of the oxalate bridge and a molecular orbital (MO) analysis^{3,4} indicates a primarily O-O through-space interaction as the principal superexchange pathway.

Azide-Bridged Complexes

Replacement of the oxalate dianion with two azide ions produced complexes of the form $[\text{Cu}_2(\text{"dien"})_2(\text{N}_3)_2](\text{Y})_2$. The magnetic susceptibility and EPR data substantiate the dimeric formulation and again the complexes having the Et₅dien ligand which enforces a TBP geometry

showed the largest antiferromagnetic exchange interaction. The bridging mode of the azide ion could not be inferred from various spectroscopic techniques, and the X-band EPR spectra revealed unusually large zero-field splittings. X-ray structural analysis of $[\text{Cu}_2(\text{Me}_5\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$ ⁵ revealed that the azide ions were bridging in a $\mu(1,3)$ fashion. The zero-field splittings greatly exceed the values calculated from purely dipolar contributions and arise from pseudodipolar interactions which have their origin in exchange interactions in excited states.

Aromatic Diamine-Bridged Complexes

The effectiveness in propagating an exchange interaction of the d_{z^2} ground state in a TBP geometry led to attempts to prepare complexes with more extended bridging groups. Complexes of the form $[\text{Cu}_2(\text{tren})_2(\text{DA})](\text{Y})_4$ were prepared, where tren is $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$, DA represents an aromatic diamine such as p-phenylenediamine (PPD) or benzi-dine (BZD), and Y^- is variously NO_3^- , ClO_4^- , or PF_6^- . Remarkably, the magnetic susceptibility data revealed relatively large exchange interactions for the PPD-bridged complexes (J varies between -19.8 cm^{-1} and -35.1 cm^{-1} depending upon the counterion) and even the BZD-bridged complexes exhibited exchange coupling (J varies from -3.3 to -4.5 cm^{-1}). In order to confirm the intramolecular nature of the interactions, the x-ray structure of $[\text{Cu}_2(\text{tren})_2(\text{BZD})](\text{NO}_3)_4$ was solved⁶ and it reveals discrete TBP binuclear cations and nitrate anions with a Cu-Cu distance of more than 12 \AA . The phenyl rings in the BZD bridge have nonzero dihedral angles and are connected by a C-C single bond. From MO calculations the principal superexchange pathway is by means of the σ framework of the BZD molecule although the low symmetry of the bridging group cannot discount a π spin polarization contribution.

Conclusions

The presence of a magnetic exchange interaction between two paramagnetic metal ions separated by an extended molecular unit provides one means of determining if that bridging group could support intramolecular electron transfer. The interface of the metal ion orbitals with those of the bridge which have the proper symmetry and energy to produce a delocalized electronic structure is a qualitatively similar situation for two metal ions which are exchange coupled or redox active. This is especially true when the precursor complex in an electron transfer reaction is in the nonadiabatic regime,⁷ i.e., a relatively long lifetime of the precursor is found relative to the rate of electron transfer. It is hoped that these studies will encourage further experimental and theoretical work involving electron-dynamical phenomena and their interrelationships.

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ELECTRON EXCHANGE ACROSS CYANIDE AND CYANIDE-LIKE BRIDGES IN COPPER (II) SYSTEMS

David S. Bieksza

Final Seminar

18 May 1978

Paramagnetic centers in transition metal cluster compounds may interact with each other by means of delocalization of unpaired electron density from one metal site to another — electron exchange. The interaction arises either from direct overlap of the metal orbitals, forming metal-metal bonds, or from superexchange through diamagnetic bridge orbitals. This delocalization causes ferro-magnetic or antiferromagnetic bulk magnetic behavior. Ferromagnetism arises from the spin alignment of unpaired electrons which occupy orthogonal orbitals. Antiferromagnetism arises from spin pairing when unpaired electrons occupy the same orbital. In either case the coupled spin states are split; for binuclear copper (II) systems a singlet state and a triplet state result. Describing the exchange interaction with a spin Hamiltonian of the form $H = -2J \underline{S}_1 \cdot \underline{S}_2$, the states are split by an amount equal to $2J$. Variable temperature magnetic susceptibility experiments can determine both the sign and magnitude of J , the exchange parameter.

Cyanide-bridged dimers were prepared of the form $(Cu_2L_4CN)(PF_6)_3$, where L is either 2,2'-bipyridine or 1,10-phenanthroline, and $(Cu_2tren_2CN)(PF_6)_3$, where $tren$ is 2,2',2''-triaminotriethylamine. These ligands were chosen on the basis that all three tend to enforce trigonal bipyramidal geometry about copper (II), as well as their ability to stabilize the metal from reduction to cuprous cyanide. Infrared spectra indicated end-to-end bridging by the cyanide in each case. In the EPR spectra only isotropic signals around $g=2.1$ were obtained, the result of exchange averaging between copper centers with misaligned g -tensor axes. Magnetic susceptibility found the exchange interaction to be antiferromagnetic for each dimer. The exchange parameters were measured to be -9.4 cm^{-1} for the bipyridine compound, -29 cm^{-1} for the phenanthroline compound, and -88 cm^{-1} for the $tren$ compound. The variation in J values arose from the varying amounts of overlap of the cyanide sigma orbitals with the copper d_{z^2} orbitals.

To determine how extended the bridge could become and still support an exchange interaction via a sigma-only pathway, dicyanamide-bridged dimers were prepared of the form $(Cu_2tren_2N(CN)_2)Y_3$, where Y is BF_4^- , ClO_4^- , PF_6^- , or $B(C_6H_5)^-$. Magnetic susceptibility found no interaction ($|J|$ less than 0.5 cm^{-1}) for all compounds except the tetraphenylborate dimer, where $J=2.5 \text{ cm}^{-1}$. The pattern was repeated in the EPR spectra: all the compounds had an isotropic derivative around $g=2.2$ except for the tetraphenylborate dimer, which had an axial spectrum. Likewise the IR and Raman spectra of the three non-interacting compounds matched each other in the cyanide region, but the spectrum of the fourth compound had different band positions and intensities. The explanation for these observations centered on the angle at the middle nitrogen of the dicyanamide bridge, ordinarily $120-130^\circ$. A larger angle, about 160° , was consistent with the EPR, IR and Raman data. Molecular orbital calculations indicated that as the angle increased overlaps both within the bridge and between bridge and metal orbitals increased, and so a more viable pathway for electron exchange was created.

PART ONE: BINUCLEAR PYRAZINE-BRIDGED COPPER(II) AND VANADYL COMPLEXES

PART TWO: CONSEQUENCES OF HYDROGEN BONDING INTERACTIONS

FOR COBALT-DIOXYGEN COMPLEXES

J. Patrick Cannady

Final Seminar

July 11, 1978

Binuclear transition metal complexes in which pyrazine serves as a coordination bridge between the two metal centers have been the subjects of much interest in recent years. Determinations of the rate of intramolecular thermal electron transfer in the so-called Creutz and Taube mixed-valence ion, $[(\text{NH}_3)_5\text{Ru-pyz-Ru}(\text{NH}_3)_5]^{5+}$, first reported¹ in 1969, have² been the focus of much discussion in the literature. In a recent report,² it was found that the unpaired electron, which is localized in a (d_{xz}, d_{yz}) orbital on the Ru(III) center, is conveyed by the pyrazine bridge fast on the ¹H NMR time scale, but slowly on the EPR timescale. However, the related bis-trivalent ion, $[(\text{NH}_3)_5\text{Ru-pyz-Ru}(\text{NH}_3)_5]^{6+}$, gave no evidence of a magnetic exchange interaction down to 4.2°K. In several polymeric copper(II) species, in which infinite $(\text{Cu-pyz})_x$ chains exist, exchange interactions have been detected, e.g., for $[\text{Cu}(\text{NO}_3)_2\text{-pyz}]_x$, $J = -7.4 \text{ cm}^{-1}$.³ Other polymeric copper(II)-pyz species, such as $[\text{Cu}(\text{hfac})_2\text{pyz}]_x$ and $[\text{Cu}(\text{hfac})_2\text{DABCO}]_x$, where hfac = hexafluoroacetylacetone and DABCO = 1,4-diazabicyclo 2.2.2 octane, have been investigated but show no evidence of a superexchange interaction down to 1.8°K.⁴ Extended Huckel molecular orbital considerations of Hoffmann and coworkers⁵ led them to conclude that both pyrazine and DABCO should be very capable of serving as σ -type pathways for antiferromagnetic superexchange.

In an effort to determine the extent to which σ - and π - type interactions could be propagated by these bridging units under the most favorable electronic conditions, a series of copper(II) and vanadyl complexes was prepared.⁶ A range of electronic ground states was obtained in this series by using $\text{Cu}(\text{tren})^{2+}$ (ground state = d_{z^2}), $\text{Cu}(\text{hfac})_2$ (ground state = $d_{x^2-y^2}$), and $\text{VO}(\text{hfac})_2$ (ground state = d_{xy}) as the one-unpaired-electron sources. EPR and magnetic studies support a binuclear formalism for these compounds. Values of the superexchange parameter, J , were most negative for the complexes $[\text{VO}(\text{hfac})_2]_2\text{B}$, where B = pyrazine ($J = -19.0 \text{ cm}^{-1}$), 2-methylpyrazine ($J = -6.7 \text{ cm}^{-1}$), and 2,5-dimethylpyrazine ($J = -4.0 \text{ cm}^{-1}$). $[\text{Cu}_2\text{tren}_2\text{pyz}](\text{ClO}_4)_4$ and $[\text{Cu}(\text{hfac})_2]_2\text{DABCO}$ gave values for J of -3.2 cm^{-1} and $< 0.5 \text{ cm}^{-1}$, respectively. Thus, the most favorable situation for superexchange via pyrazine appears to arise from the interaction between the π orbitals of pyrazine and the d_{xy} orbitals on the V centers. This is made geometrically plausible by assuming an equatorial coordination of the pyrazine in the vanadyl complexes. σ -type interactions in these systems are seen to be very weak or not existent. Nevertheless, solution studies on $\text{VO}(\text{hfac})_2 \cdot 2\text{pyz}$ in methylene chloride indicate a decrease of almost three orders of magnitude for the equilibrium constant for binding the second $\text{VO}(\text{hfac})_2$ unit over that for binding the first to pyrazine. This marked decrease in the basicity of the pyrazine nitrogen provides an example in which it is apparent that the consequences of a weak coupling of the electronic manifolds of the two metal centers does not entirely account for the total effect that the two metal centers can have on each other.

PART TWO

Hydrogen bonding has been invoked to explain the enhanced rate of formation at ambient temperatures of the binuclear peroxo bridged species, $\text{LPCoO}_2\text{CoPL}$, where P = protoporphyrin IX dimethyl ester and L = imidazole, in toluene over solutions in which L = N-methylimidazole, which is incapable of serving as a hydrogen bonding acid. In order to investigate the generality of this effect for other cobalt-dioxygen systems, experiments were undertaken on a system which should better lend itself to investigation of this type. CoSMDPT, where SMDPT = N-methyl-3,3'-bis(salicylideneamino)-bispropylamine, has been shown by EPR to bind dioxygen reversibly at low temperatures as well as at ambient temperatures.^{8,9} ^1H and ^{19}F NMR studies on benzene, toluene and methylene chloride solutions of CoSMDPT to which TFE, 2,2,2-trifluoroethanol, has been added indicate that TFE interacts with CoSMDPT, either by hydrogen bonding to the phenolic oxygens or the imine linkage of the ligand. Exposure to dioxygen results in the formation of a diamagnetic species. EPR studies show that the room temperature signal of the 1:1 Co- O_2 adduct is decreased upon addition of TFE to a toluene solution of CoSMDPT under oxygen. Low temperature and frozen glass EPR parameters do not show much dependence on the presence of TFE. However, spectrophotometric measurements of the 1:1 equilibrium constant for the binding of dioxygen to CoSMDPT in toluene and methylene chloride with and without TFE do show a marked dependence on the presence of TFE. In general, K_{O_2} increases on going from toluene to methylene chloride. However, the presence of TFE in toluene solutions results in a decrease in K_{O_2} , while in methylene chloride, a marked increase is observed. The interplay between solvation and hydrogen bonding effects in these systems is seen to account for these behaviors.

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REACTIVITY OF POLYSTYRENE-BOUND BIPYRIDINE AND THE CATALYTIC POTENTIAL OF ITS TRANSITION METAL COMPLEXES

Anton El A'mma

September 21, 1978

Since 1971, there has been a growing interest in catalysis by solid supported transition metal complexes.¹ The metal complex which is grafted onto a support can either be an established homogeneous catalyst or its metal center could acquire catalytic activity after the process of heterogenization.

Crosslinked polystyrene is a commonly used solid support and numerous ligands have been anchored to this resin through covalent bonds. The resin which is functionalized with the analog of tri-phenylphosphine²⁻⁴ is known to heterogenize potent homogeneous catalysts. However it has the following drawbacks: 1, air sensitivity of the phosphorus center; 2, lability of phosphine-metal linkage in some systems; 3, polymer crosslinking induced by the complex which modifies the primary structure of the support.

In order to bypass the above disadvantages, we have independently undertaken a study of the reactivity of a polymer bound bipyridine [(P)-Bipy] reported by Neckers et al.⁵ and investigated the catalytic activity of some of its transition metal complexes towards hydrogenation. The choice of immobilized bipyridine stems from the fact that this ligand stabilizes a wide range of metal oxidation states and functions as a chelate.

The bonding properties of (P)-Bipy were studied by reacting it with a series of carbonyl containing metal complexes and then comparing the IR spectra (C-O stretching region) of the various polymer attached products with those of compounds derived when bipyridine undergoes the corresponding reactions. Polymer bound pyridine was used in similar reactions to ascertain the bidentate behavior of (P)-Bipy. Thus, (P)-Bipy was reacted with Mo(CO)_6 , $(\text{CO})_2\text{RhCl}/2$, and $(\text{CO})(\text{PPh}_3)\text{RhCl}/2$ to form (P)-Bipy Mo(CO)_4 , [(P)-Bipy $\text{Rh(CO)}_2\text{Cl}$, (P)-Bipy RhCOCl] and (P)-Bipy $\text{Rh(PPh}_3\text{)Cl}$ respectively. The further reaction of (P)-Bipy Mo(CO)_4 with PPh_3 generated (P)-Bipy $\text{Mo(CO)}_3(\text{PPh}_3)$. These investigations indicate that (P)-Bipy functions as a bidentate ligand.

Catalytic hydrogenations were observed with the following catalyst precursors: (P)-Bipy PtCl_2 , (P)-Bipy PdCl_2 , polystyrene dispersed palladium metal and (P)-Bipy $\text{Rh(PPh}_3\text{)Cl}$. The system (P)-Bipy PtCl_2 shows a high degree of selectivity towards the hydrogenation of terminal olefinic bonds. The material (P)-Bipy PdCl_2 reduces a wide variety of coordinating and non-coordinating substrates (with isomerization where applicable) and polymerizes methyl acrylate. The activity of this catalyst can be attributed in part to the presence of metallic palladium. Polystyrene dispersed palladium was found to be a factor of 2-3 times slower (rate of H_2 uptake) than 5% Pd/C in hydrogenating p-benzoquinone and nitrobenzene. This system (P)-Bipy $\text{Rh(PPh}_3\text{)Cl}$

is even more effective in hydrogenating internal and terminal double bonds than (P)-BipyPdCl₂. Tentative mechanisms are discussed for the activity of both (P)-BipyPtCl₂ and (P)-BipyRh(PPh₃)Cl. All of the above catalyst precursors have been reused without any loss of activity.

In summary, the use of immobilized bipyridine has facilitated the understanding of the coordination sphere of the grafted metal complex and generated some novel hydrogenation catalysts.

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The flexibility offered by the use of molecular cavities has excited much interest in spite of the added complications involved with their application. Zeolites,¹ silicates,² and graphite³ represent long-standing examples of exploitation of cavities for various applications. The quest for solution phase cavities is satisfied, at least in part, with cyclodextrins,^{4,5} sugar derivatives, and cryptands,^{6,7} synthetic multicyclic heteroatom compounds. The purpose of this seminar is to review some properties and selected examples of the use of molecular cavities, some of which are large enough to contain substituted aromatics and others which can only include small molecules and metal ions.

SMALL CAVITIES

Most of the research with cryptands has dealt with the bicyclic compounds such as $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N$ denoted as [2.2.2], although other topologically different derivatives are known. Early research showed that [2.2.2] prefers to include the potassium cation while [3.3.2] exhibited nearly equal formation constants for potassium and rubidium cations. The observed stability was described in terms of the number and type of binding sites leading to the "cryptate effect" while the selectivity was seen to be a function of the fit of cavity size with the metal cation size.⁸ The temperature dependence of the complex formation showed that the change in enthalpy reflected the selectivity of a particular cryptand.⁹ In methanol, both selectivity and stability of the included complexes were enhanced.^{8,9} It was observed that, in methanol, the alkaline-earth complex with the greatest stability also possessed the greatest activation enthalpy for dissociation.¹⁰ Similar characteristics were also observed with alkali cations¹¹ and it was suggested that the transition state for formation of the complex closely resembles the state of the reactants.^{10,11} The energy of desolvation of the metal cation would be compensated by interaction with the complex.

Recent applications of small cavities have included the preparation of inert lanthanide cryptates,¹² stabilization of the sodium anion,^{13,14} and use in forming isolated counter-ions.¹⁵

LARGE CAVITIES

A convenient source of large cavities is provided by the cyclodextrins which are α -1,4-linked cyclic oligomers of D-glucopyranose (α , β , and γ refer to 6, 7 and 8 glucose units, respectively) which form a hollow, hydrophobic, truncated cone ringed by twelve secondary hydroxyl functions at the large end, and six primary hydroxyl functions at the other end.¹⁶ A wide variety of molecules can be included into cyclodextrins resulting in many suggestions for the driving force for inclusion. Nuclear magnetic resonance¹⁷ and crystal structure determinations¹⁸ have been employed to examine the nature of the binding and orientation of included benzoic acid and sodium benzoate. These studies have

shown that in both cases the acid function is located inside the cavity. A comprehensive model of the thermodynamics of inclusion of aquated apolar substrates was recently reported.¹⁹

The applications of cyclodextrins have been numerous: the resolution of chiral sulfinyl compounds,²⁰ the preparation of Vitamins K₁ and K₂,²¹ and catalytic hydrolysis of amides.²² Furthermore, the substrate binding by enzymes can be modeled with cyclodextrins or derivatives.^{23,24}

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Intervalence Electron Transfer in Mixed Valence Compounds

Bruce C. Bunker

Final Seminar

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Experiments aimed at understanding the energetics and rates of intervalence electron transfer in a variety of mixed-valence compounds have been undertaken to try to obtain a data base for testing current theories regarding more general electron transfer phenomena. These theories can be applied in areas of chemistry and physics ranging from electrochemistry to semiconductor science. In particular, an attempt has been made to check the validity and/or the limitations of the Hush theory¹, which relates the energy of the intervalence transfer band observed in the electronic spectrum to the energy of the thermal barrier to intervalence electron transfer within the mixed-valence compound.

Part of the research effort has been directed at studying mixed-valence compounds which show behavior which might be indicative of a breakdown in the Hush theory. One such compound is the mixed-valence [2,3] oxidation state of the dimer μ -pyrazine-bis(pentaammineruthenium) tosylate, which contains one Ru(II) and one Ru(III). Since Creutz and Taube² first reported the synthesis of this dimer in 1969, it has been the subject of a great deal of interest and controversy in the literature. It exhibits an intervalence transfer band which has neither the band width nor the solvent dependence predicted on the basis of the Hush theory. The many attempts which have been reported to experimentally determine the rate of intervalence electron transfer have led to ambiguous results.

To further our understanding of this compound and the Hush theory, we conducted experiments³ to help us formulate a description for the molecular orbitals involved in the electron transfer and to determine the rate of intervalence electron transfer between the two metal centers. Variable temperature magnetic susceptibility results on the [3,3] pyr dimer coupled with low temperature EPR results for both the [2,3] pyr and [3,3] pyr dimers indicate that the odd electron in the dimer resides in the (d_{xz}, d_{yz}) orbital set on the Ru(II) center and is not in a molecular orbital which is delocalized over both metals as postulated by Hush⁴. Variable temperature studies

indicate that in solution the rate of electron transfer from the Ru(II) center to the Ru(III) center is fast on the NMR time scale of 10^{-5} sec from room temperature down to -80°C . It is slow on the EPR time scale of 10^{-9} sec in the solid state at all temperatures below -50°C . If outer coordination sphere effects are assumed to be negligible, then these EPR and NMR results can be used to bracket the magnitude of the thermal energy barrier to between 3.4 and 6.7 kcal/mole. This is in agreement with the Hush theory prediction of 4.5 kcal/mole, which is based on the energy of the IT band. However, it may be that in the solid state, outer coordination sphere effects dominate, and that lattice effects can lock the odd electron onto one valence site.

The other part of this research effort concerning mixed-valence compounds has been focused on trying to develop better experimental techniques for studying the intervalence electron transfer phenomenon. The technique which has been investigated most extensively is time domain reflectometry, or TDR^{5,6}. This technique can be used to study the dielectric relaxation properties of samples in the frequency range from 10^6 Hz up to 10^{10} Hz. The charge oscillations associated with intervalence electron transfer can give rise to such dielectric relaxation. Analysis of TDR data can yield the relaxation frequency associated with the relaxation process, which can be used to calculate the rate of electron transfer. Variable temperature TDR data can be used to calculate the magnitude of the thermal energy barrier to electron transfer by using the Arrhenius equation.

TDR data has been obtained for a sample of europium sulfide which analyzes as Eu_4S_5 . Analysis of the data indicates that the rate of electron transfer in this mixed valence compound is $2.2 \times 10^9 \text{ sec}^{-1}$ at room temperature, and that the magnitude of the thermal energy barrier to the electron transfer process is around 920 cal/mole. This barrier corresponds almost exactly to the band gap energy associated with the semiconductivity of the compound. This has been determined from IR measurements, where the edge of the band gap absorption feature can be observed at around 320 cm^{-1} . These results represent the first reported use of time domain reflectometry on solid samples, and the first time the technique has been used to

determine the rate of electron transfer in a mixed valence compound.

Other mixed-valence compounds have also been studied. Magnetite, or Fe_3O_4 , exhibits a rapid relaxation process which appears to be fast on the TDR time scale. This result is consistent with Mossbauer results which have been obtained for the compound⁷. Soluble Prussian blue exhibits a relaxation process which is observable in the TDR, but is slow on the TDR time scale of 10^{-6} sec, which also agrees with the Mossbauer results⁸. No relaxation is observed for solid $\left[\left((\text{NH}_3)_5\text{Ru} \right)_2\text{pyr} \right]^{5+}$ tosylate. This is consistent with the EPR study³ which indicates that the odd electron in the dimer is localized on one metal center in the solid state. The mixed-valence trimer $\text{Fe}^{2+}\text{Fe}_2^{3+} \text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_5$, reported by Gol'danskii⁹ to exhibit dynamic electron transfer on the Mossbauer time scale, has also been studied. It does not exhibit the expected dielectric relaxation in the TDR, nor do several other mixed-valence oligamers which have been studied. It is currently not known whether this means that the TDR technique is only sensitive to electron transfer in extended lattice systems, or that literature estimates of electron transfer rates are incorrect for these systems.

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PHOTO-OXIDATION OF INORGANIC COMPOUNDS
WITH APPLICATION TO SOLAR ENERGY

Richard W. Wegman

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Thermal conversion and quantum conversion are two fundamental ways for converting solar energy into useful energy. A thermal system utilizes a collector that transforms light energy into heat.¹ The heat is transferred to a thermal storage system for use at a later time. Quantum conversion utilizes the available solar energy to induce a photochemical or photoelectric process in the absorbing material. In a photochemical process the absorber is activated to an excited state by the absorption of light. The energy gained by the absorber is lost by deactivation of the excited state through radiative and non-radiative decay processes.² An energy storage system coupled to the excited state provides an alternative deactivation pathway by directing the excess energy into a process that produces a stable fuel.³ The efficiency of the energy storage process is limited by certain thermodynamic and kinetic parameters of the absorbing system. The thermodynamic limitations include:

- 1) The maximum chemical potential difference achievable between the ground and excited state;⁴ and
- 2) Power drainage into the storage system and its effect on the photo-generated chemical potential.⁵

The kinetic limitations arise from the inherent microreversibility of the system.⁶

The photo-dissociation of water into O_2 and H_2 is a very attractive system for solar energy conversion.⁷ Hydrogen is an excellent fuel and the source is cheap and plentiful. Unfortunately, high energy photons, not abundant in solar radiation, are required for direct photo-decomposition of water. Chemical systems that photo-catalytically decompose water by utilizing lower energy photons are therefore necessary. One of the oldest known systems involves the photo-oxidation of $Ce(III)$ to $Ce(IV)$ in dilute perchloric acid solution.⁸ The process begins with the photo-excitation of $Ce(III)$ to $*Ce(III)$. The $*Ce(III)$ ion reduces H^+ resulting in the production of H_2 gas and $Ce(IV)$. The system is cyclic because $Ce(IV)$ is capable of oxidizing water to regenerate H^+ and $Ce(III)$.

A similar system involves the photo-oxidation of $Cu(I)$ to $Cu(II)$ in the presence of H^+ .⁹ This process is non-cyclic because $Cu(II)$ cannot oxidize water to regenerate starting materials. A mechanism for H_2 production in this system has recently been proposed.¹⁰

The photo-excitation of $Ru(bpy)_2^{2+}$ to $*Ru(bpy)_2^{2+}$ and the consequent reduction of water by $*Ru(bpy)_2^{2+}$ has been suggested as a plausible method for water decomposition.¹¹ Apparently, for kinetic reasons, the electron transfer process is too slow to compete with excited state decay. Recently, Meyer¹² has reported a working

photo-electrochemical cell utilizing $\text{Ru}(\text{bpy})_3^{2+}$. The cathode is a solution containing $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ in 1 N H_2SO_4 . The anode is a solution containing $\text{Fe}(\text{II})$ and $\text{Fe}(\text{III})_2^{3+}$ also in 1 N H_2SO_4 . Photolysis of the cathode produces $^*\text{Ru}(\text{bpy})_3^{2+}$ which is oxidized by $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ to give $\text{Ru}(\text{bpy})_3^{3+}$. A current is produced by the oxidation of $\text{Fe}(\text{II})$ by $\text{Ru}(\text{bpy})_3^{3+}$.

The photochemistry of di-nuclear metal complexes is of current interest and recently a rhodium¹³ and several molybdenum di-nuclear compounds^{14,15} have been shown to stoichiometrically reduce H^+ to H_2 during photolysis.

The systems developed thus far have inherent problems which render them inadequate for the practical production of fuels. These problems include:

- 1) High energy excitation wavelengths;
- 2) Low quantum yields in the conversion process;
- 3) Non-cyclic systems.

Research oriented towards the engineering of systems capable of working at a practical level is necessary.

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DYNAMICS OF ELECTRONIC SPIN TRANSITIONS IN IRON "SPIN-EQUILIBRIUM" SYSTEMS

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Introduction

Many iron(II) and iron(III) complexes exhibiting properties characteristic of the high-spin--low-spin crossover region have been reported.¹ Most of these studies have focused on two questions: 1) What types of ligands give rise to such behavior? and 2) How does variation of ligand substituents affect the position of the equilibrium? Only very recently has there been significant progress in answering a fundamental yet more difficult question, namely, what are the kinetics and mechanisms of spin state interconversions? Spin transitions are believed to play an important role in biological systems, and spin equilibria in certain hemoproteins may be coupled to electronic transport.² Essential to an assessment of the role of spin multiplicity changes in naturally occurring processes is an understanding of their dynamics in model systems.

Solution State

Spin transitions for isolated molecules may be viewed as inter-system crossing processes involving nonadiabatic electron transfer between two electronic isomers possessing distinct nuclear geometries.³ For systems in solution, magnetic data yield approximately linear $\log K$ vs. $1/T$ plots, consistent with a dynamic equilibrium. The "spin-flipping" rate has been measured directly for a number of complexes by the stimulated laser Raman T-jump technique.³ These solution data generally indicate slower rates for those transitions involving greater changes in the metal-ligand bond lengths. Nonbonding intraligand steric interactions and multidentate chelation⁴ have been shown to retard the reorganization of the primary coordination sphere. In the absence of such stereochemical restraints, accelerated rates controlled by electronic factors are observed. Partial quantum-mechanical mixing of the states increases the rate of nonadiabatic electron transfer, with covalent bonding, especially to pi-acceptor sulfur ligands, leading to the fastest rates. Most recently, more accurate ultrasonic relaxation measurements at several temperatures have yielded estimates in the range 10^{-2} to 10^{-3} for the transmission coefficient for the spin-forbidden intersystem crossing in $[\text{Fe}^{\text{II}}(\text{HB}(\text{pz})_3)_2]$, $[\text{Fe}^{\text{II}}(\text{paptH})_2]^{2+}$, and $[\text{Fe}^{\text{III}}(\text{Sal}_2\text{trien})]^+$.^{5,6}

Solid State

"Spin-equilibrium" compounds in the solid state seldom give linear plots of $\log K$ vs. $1/T$ and their physical properties cannot be readily interpreted in terms of independently acting molecules. Thermally incomplete transitions due to "residual paramagnetic impurities",^{1b} "plateaus" due to "lattice effects of unknown origin",⁴ abrupt phase transitions,⁷ thermal hysteresis,⁸ and marked dependence of the position and nature of the "equilibrium" on counter ion^{1b} and solvation effects⁹ have intrigued and bewildered many workers.

Several lines of evidence suggest that spin transitions in the solid state are cooperative in nature, with significant coupling between the electronic states and lattice vibrations:

1) In $[\text{Fe}^{\text{III}}(\text{phen})_2(\text{NCS})_2]$, which undergoes an almost discontinuous spin transition, heat capacity measurements reveal a λ -type phase transition accompanied by an entropy change far greater than can be accounted for by magnetic and configurational entropy alone. Infra-red spectra throughout the transition region show two coexisting spin states, each characterized by a constant 10 Dq value.⁷

2) In $[\text{Fe}^{\text{II}}(4\text{-CH}_3\text{-phen})_2(\text{NCS})_2]$, which exhibits a continuous transition over a 125° range, the Debye-Waller factor for each spin state shows deviations from the Debye model, but only when the site fraction of that particular state drops below a limiting value.^{10, 11} The nature of these deviations is taken as evidence for the formation of domains of the minority spin state. Further evidence for the presence of domains is provided by an ESCA study of $[\text{Fe}^{\text{II}}(6\text{-MePy})_3\text{tren}]\text{PF}_6$.¹²

3) Mössbauer studies¹³ show that the transition temperature, T_C , for the gradual spin multiplicity change in mixed crystals of $[\text{Fe}_x\text{Zn}_{1-x}(2\text{-pic})_3]\text{Cl}_2 \cdot \text{C}_2\text{H}_5\text{OH}$ decreases with dilution of the ferrous ion, consistent with a smaller total enthalpy change for lower concentrations.

4) The pronounced hysteresis ($\Delta T_C = 34^\circ$) seen for $[\text{Fe}(\text{papth})_2](\text{NO}_3)_2$ has made possible a unique Mössbauer kinetic study of the high-spin to low-spin transition rate.⁸ Extrapolation of the data to 298K yields a rate 2×10^6 times slower than that observed in solution. Extrapolation to 105K yields a spin lifetime of 19 years! These results show that thermally incomplete transitions are merely kinetically controlled non-equilibrium systems.

The observations are all consistent with a static mechanism for the solid state. Occasional thermal excitations induce localized molecular distortions which are "communicated" throughout the lattice via long-wave phonons to form domains which may eventually combine. The strength of the coupling determines the sharpness of the transition.^{10, 11}

Fundamental unanswered questions concern the mechanisms of spin interconversion for 1) the extensively studied ferric dithiocarbamates¹⁴ and a few other systems¹⁵ which appear to be dynamic equilibria in solids, and 2) those rare systems which show continuously varying 10 Dq over the transition region.¹⁶ Also of interest is the possibility of coupling of the phonons of a dense medium^{17, 18} with the "dynamic" spin transitions in solutions. Finally, the relevance of these studies of spin transition dynamics to biological systems is briefly considered.¹⁹⁻²¹

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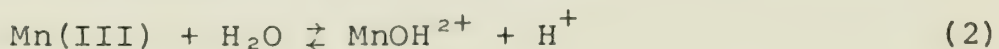
Because the hexaaquo manganese(III) ion is very unstable toward disproportionation



and reduction ($E^\circ \approx 1.5$ volts) in water at neutral pH, aqueous Mn(III) species are not well known. Recently, however, the importance of Mn(III) complexes in biological and environmental systems has been postulated and in some cases verified. For these reasons, inorganic chemists have recently begun looking in earnest for stable manganese(III) complexes in order to explore the chemistry of these little-known species. Because complexes of Mn(III) with oxygen donor ligands appear to be the most important in biological systems and because they have been the most widely studied, the present discussion will be limited to these species.

Three recent reviews^{1,2,3} describe how manganese(III) can be stabilized with respect to disproportionation and reduction in aqueous solution. Disproportionation can be prevented by the use of H^+ and Mn(II) to shift the equilibrium (see equation 1) toward the left or by complexing the manganese(III) with non-oxidizable ligands to prevent autoredox. The Mn(III)/Mn(II) couple is a measure of the stability of the Mn(III) complexes and some ligands can lower this reduction potential by as much as 0.7 volt.¹ This decrease in reduction potential allows manganese(III) complexes to exist in aqueous solution.

Besides thermodynamically stabilizing Mn(III) toward reduction, certain ligands lower the kinetic lability of Mn(III).⁴ This effect is demonstrated by a kinetic study in which pyrophosphate competes effectively with the oxidizable substrate iso-propyl mandelate for a binding site on Mn(III).⁵ The iso-propyl mandelate must bind to the Mn(III) in order to be oxidized and released as benzaldehyde. Work by Jones and Hamm⁴ and Pelizzetti, *et al.*⁶ shows that the reduction of manganese(III) is inhibited by H^+ ions and chelating ligands which is often observed for trivalent transition metal ions. The H^+ ion effect is due to the equilibrium shown below:



The MnOH^{2+} is often a more reactive species toward reduction than hexaaquo Mn(III) so the forward reaction will be enhanced by higher pH. Strong complexing species affect the lability of Mn(III) toward reduction as shown in the following example:



When a strong chelating ligand is present, the reverse reaction becomes more favorable with respect to the forward reaction since the more highly charged Mn(III) can form stronger complexes than Mn(II).

From these examples, one sees that factors affecting thermodynamic stability of Mn(III) toward reduction may be the same factors that affect kinetic lability of these complexes.

The manganese(III) gluconate complex prepared by Sawyer and coworkers is both kinetically and thermodynamically stable toward oxidation and reduction even in the presence of hydrogen peroxide.⁷ This complex exists in a monomer-dimer equilibrium as shown by polarography, absorption spectra and magnetic susceptibility measurements.^{8,9} In the monomer form it is stable in the presence of oxygen, while the binuclear species is oxidized to give the manganese(IV) complex. The monomeric gluconate complex is the most stable toward reduction of the many complexes of manganese(III) prepared by D. T. Sawyer and coworkers. This group has also characterized a large group of complexes with other polyhydroxy ligands using polarography and magnetic susceptibility experiments.¹⁰ The relevance of their work to plant photosynthesis has been summarized along with recommendations for obtaining a reasonable inorganic model for photosystem II.¹¹

Photosystem II is the biological system receiving the most attention with respect to manganese(III). Proton relaxation studies on this system show that the manganese atoms in the Mn-enzyme of photosystem II exist in several oxidation states both in the resting and in the active enzyme.¹² While manganese(III) is likely one of the oxidation states present in photosystem II, more conclusive evidence exists for its presence in two other biological systems. The enzyme manganosuperoxide dismutase was shown to contain Mn(III) in the resting state by epr and magnetic measurements on the purified enzyme.¹³ Resonance Raman spectra show that manganese(III) can be substituted for Fe(III) in ovo- and human serum transferrins.¹⁴

Manganese(III) complexes also appear to play an important role^{15,16} in the complicated chemistry of manganese in soil and surface waters^{17,18,19} although further work is needed. Since Mn(II) and Fe(III) form stable outer sphere and inner sphere complexes with fulvic acids respectively,²⁰ it is reasonable that Mn(III) might also be stabilized by fulvic acids in natural waters. This possibility could be tested using water proton nmr line widths in studies similar to those reported by Gamble, Langford and Tong.²⁰

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THERMOCHROMIC BEHAVIOR OF SELECTED INORGANIC SYSTEMS

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The relationship between the color and structure of inorganic coordination compounds has generated interest in the study of the phenomenon known as thermochromism. Thermochromism has been defined as the reversible change in the color of a compound which has been either heated or cooled.^{1,2} Observations have shown that this color change may occur either gradually, characteristic of continuous thermochromism, or abruptly, characteristic of discontinuous thermochromism. More specifically, the thermochromic behavior of inorganic systems has been attributed to either (1) a change in the ligand geometry of a coordination complex, (2) a temperature dependence of the line widths of electronic absorption bands, (3) a variation in the number of solvent molecules in the coordination sphere of a solvated metal ion or (4) a shift in an equilibrium between two different molecular structures.²

Much of the recent research in the area of thermochromic inorganic compounds has been centered around the N,N-diethylethylenediamine complexes of copper(II)³⁻⁷ and nickel (II)^{3,8} salts. Pfeiffer and Glaser,⁹ in the course of their preparative work with copper salts of complex nitrogen ligands, discovered the copper(II) perchlorate salt of the bidentate ligand, N,N-diethylethylenediamine(diäten, $\text{H}_2\text{NCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$), was thermochromic. The early work of these investigators was later modified by Lever, et al.,⁴ who succeeded in preparing two additional thermochromic compounds, $\text{Cu}(\text{diäten})_2(\text{BF}_4)_2$ and $\text{Cu}(\text{diäten})_2(\text{NO}_3)_2$. The observed color change for each of these compounds was from red to violet as the temperature was increased. Analogous $\text{Ni}(\text{diäten})_2\text{X}_2$ complexes have also been prepared,^{3,8} where $\text{X} = \text{I}, \text{ClO}_4, \text{BF}_4, \text{NO}_3, \text{Br}, \text{AgI}_2, \text{PbI}_3, \frac{1}{2}\text{HgI}_4, \text{and } \frac{1}{2}\text{CdBr}_4$. All of the nickel complexes were found to be thermochromic changing color from orange-yellow to bright red at elevated temperatures.

The nature of the thermochromic behavior of both the copper and nickel compounds was investigated using a variety of techniques, including: infrared spectroscopy,^{4,6} differential scanning calorimetry,³ EPR spectroscopy⁵ and magnetic susceptibility.⁴ It was determined from these experiments that the thermochromic transitions resulted from increased axial interaction between the metal-nitrogen cationic species and the anionic species of the given complexes.³⁻⁶ It was noted that this increase in axial perturbation correlated well with an observed decrease in the infrared stretching frequencies of the metal-nitrogen bonds.⁴ In addition, differential scanning calorimetric data confirmed the observations of discontinuous thermochromism for the complexes, $\text{Cu}(\text{diäten})_2\text{X}_2$, $\text{X} = \text{BF}_4, \text{ClO}_4$ and NO_3 and $\text{Ni}(\text{diäten})_2\text{X}_2$, $\text{X} = \text{BF}_4$ and ClO_4 . The other compounds, with the exception of $\text{Ni}(\text{diäten})_2(\text{NO}_3)_2$ which decomposed before its transition temperature was reached, were continuously thermochromic. These results were explained in terms of anion polarizability.³

The partially substituted ammonium salts of the tetrachlorocuprate¹⁰⁻¹⁵ and tetrachloronickelate¹⁶ anions have also received attention because of their thermochromic behavior. The copper salts studied were prepared by the method of Remy and Laves,¹⁷ who obtained crystalline compounds by mixing $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with the appropriate amine hydrochloride in alcoholic solution. From a number of X-ray studies^{11,13,18-21} on these copper complexes, it was determined that the symmetry of the tetrachlorocuprate anion ranged from tetrahedral²² to square planar.¹³ However, the most stable of the possible symmetries for the CuCl_4^{2-} anion was D_{2d} .¹⁸⁻²² The change in the color of most of these compounds was directly related to the degree of distortion of the CuCl_4^{2-} anion away from D_{2d} symmetry. This fact led to attempts at correlating the amount of anion distortion with observed electronic absorption spectra.^{10,12} Also, a pressure study was made to determine if these distortions could be induced by another method.¹⁴ During the course of one study,¹⁰ it was found that the compound, (dimethylammonium)₃ CuCl_5 , although thermochromic, did not undergo any type of structural distortion, but rather was thermochromic because the electronic band widths were temperature dependent.

The nickel ammonium salts have been prepared only very recently from high temperature melts produced in sealed tube reactions.¹⁶ Complete single crystal X-ray data were not obtained for the nickel compounds, but from the preliminary powder data results the low temperature form was believed to be a distorted octahedral polymer with bridging halogens, while the high temperature form was thought to contain discrete NiCl_4^{2-} anions with tetrahedral geometry. It was also found that the nature of the cation in these complexes and its ability to interact with the anion, particularly the ability to hydrogen bond and whether the amine was partially substituted with alkyl or aryl groups, could alter the thermochromic characteristics of the complexes.¹⁶ Here, the change in the color of the compounds resulted from the change in the ligand geometry of the NiCl_4^{2-} anion as the temperature was varied. Discontinuous thermochromism was apparent for all of these ammonium nickel salts.

Lastly, thermochromic behavior has been observed for solutions of anhydrous CoCl_2 in water, methanol, 1-propanol, 2-propanol and acetone.²³ Dramatic changes in the colors of these solutions occurred when the temperature was lowered. These effects were a result of a change in the configuration of the solvated cobalt complexes from a high temperature tetrahedral form to a low temperature octahedral form.

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PHYSICAL PROPERTIES OF THE ONE-DIMENSIONAL CONDUCTING MATERIAL
BaVS₃: ITINERANCY AND STOICHIOMETRY

Jeff Kelber

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"One-dimensional" (1-d) materials may be defined as materials in which the magnetic and electronic interactions are much larger along one crystallographic axis than the other two. Such materials are of theoretical interest¹ as physical approximations of 1-d magnetic lattices, and of technological interest as possible prototypes of high temperature superconductors.^{2,3}

The 1-d materials most studied to date³ - TTF-TCNQ and derivatives, and the partially-oxidized Krogmann's salts - manifest a lattice instability, termed a Peierls distortion,^{3,4} thought to be inherent in all 1-d partially-filled band systems. This instability results in the formation of a superlattice along the unique crystallographic axis, and the opening of a band gap at the fermi surface, destroying the metallic state. Much research is now being directed towards synthesizing and characterizing new 1-d metals in order to learn more about the physics of the Peierls distortion and other 1-d cooperative phenomena.

The room temperature structure⁵ of BaVS₃ is hexagonal (P6₃/mmc), with chains of face-sharing VS₆ octahedra running parallel to the c-axis and barium atoms separating the chains. BaVS₃ undergoes a distortion to orthorhombic symmetry⁵ at lower temperature. The intrachain V-V distance⁵ (2.805 Å) is short enough that one expects metallic interaction along the vanadium chains.⁶ BaVS₃ is structurally quite different from TTF-TNQ and the Krogmann's salts, which consist of planar complexes stacked perpendicular to the unique axis. BaVS₃ is composed of chains of metal atoms bridged by sulfur ligands and may therefore be expected to reveal new aspects of 1-d cooperative phenomena.

BaVS₃ can be synthesized by either of the following methods:^{5,7}

- (1) $\text{BaCO}_3 + \text{V}_2\text{O}_5 \xrightarrow[\Delta]{\text{H}_2\text{S}} \text{BaVS}_3 \text{ (powder)}$
- (2) $\text{BaS} + \text{V} + 2\text{S} \xrightarrow[\Delta]{\text{vacuum}} \text{BaVS}_3 \text{ (powder)}$

Ferromagnetic BaVS₃ is characterized⁷ by a Curie temperature near 16K, and a magnetic moment in the ordered phase of ~0.2 Bohr magnetons (μ_B)/vanadium. Annealing this material in the presence of sulfur⁷ gradually alters the material to structurally similar antiferromagnetic BaVS₃. Further annealing with sulfur produces no further change in the sample or its magnetic properties. (The process can be reversed by annealing in the absence of sulfur). The antiferromagnetic state can also be synthesized directly by: (1) using long reaction times⁸ or by (2) with an excess of sulfur, and analysis indicates that the antiferromagnetic material is stoichiometric BaVS₃.^{7,8}

Nonstoichiometric BaVS_3 ,⁷ is also characterized by anomalies in the resistivity near 16K, 70K, and 150K, and a lattice distortion temperature of $\sim 150\text{K}$. Stoichiometric BaVS_3 is characterized^{7,8} by an electronic transition and a broad maximum in the magnetic susceptibility near 70K and a lattice distortion temperature of $\sim 250\text{K}$. An ESR signal ($g \approx 1.90$) is observed only in nonstoichiometric BaVS_3 .⁷

Recent neutron diffraction measurements confirm that:

- (1) stoichiometric and nonstoichiometric BaVS_3 are structurally distinct (though similar);
- (2) the low moment observed in the nonstoichiometric material is not due to ferrimagnetism;
- (3) No long range magnetic order occurs in stoichiometric BaVS_3 above 8K.

An itinerant electron model, with localized electrons trapped at lattice defects coupling through the itinerant vanadium 3-d electrons (a modified RKKY interaction⁹) qualitatively explains the experimental data.

The possibility of itinerancy in the BaVS_3 system is exciting because: (a) the lattice distortion is not coupled to the major electronic transition (near $\sim 70\text{K}$), and so would not seem to be the Peierls distortion expected for a d^1 system with (formally) one unpaired electron per vanadium site; and (b) all other known metal halides and oxides with the BaVS_3 structure are insulators.^{8,10}

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SOME RECENT DEVELOPMENTS IN THE INTERCALATION CHEMISTRY
OF THE LAYERED TRANSITION METAL DICHALCOGENIDES

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Interest in the layered transition metal dichalcogenides originally derived from their highly anisotropic transport properties¹. There are more than forty such compounds known², chiefly (although not exclusively) dichalcogenides of the early transition metals.

As in the case with other layered materials such as graphite³ and sheet silicates⁴, certain atoms and molecules may be intercalated into the interlamellar spaces of Group IV B and Group V B dichalcogenides².

Intercalation complexes of alkali and transition metal atoms in Group IV B VB disulfides and diselenides are of current interest as possible electrode materials in high energy density batteries⁵. Host-guest bonding in these complexes is generally thought⁶ to proceed with nearly complete electron transfer from guest to host.

Molecular species which form intercalation complexes with layered transition metal disulfides and diselenides are mostly nitrogenous Lewis bases⁷. The bonding in these complexes was postulated from the first to involve "electron donation" from guest to host, but in the usual covalent sense of coordination complex formation¹. Recent evidence for redox and ionization processes occurring in these complexes appears to apply only to ammonia⁸. Attempts to elucidate the details of bonding led to numerous structural studies, in which such techniques as powder⁹ and single crystal^{10, 11} x-ray diffraction, single crystal neutron diffraction¹², wide-line NMR¹³, and incoherent inelastic neutron scattering¹⁴ have been employed to reveal patterns of guest orientation in the interlamellar spaces of the host and to piece together a bonding scheme which involves lone pair donation into the unfilled chalcogen valence band and which suggests that interactions among guest molecules can be important.

Dines¹⁵ has recently advanced the argument that host-to-guest π -backbonding is also important in the formation of intercalation complexes by preparing and characterizing alkyl isonitrile intercalates of TiS_2 and TaS_2 . In this connection, some early work in the field with phosphines⁷ bears re-examination and, perhaps, repetition and extension. In any case, the bonding in the "molecular" intercalation complexes, even for such a simple intercalate as ammonia, cannot be considered a solved puzzle.

Another class of compounds recently added to the list of those which will intercalate into layered transition metal dichalcogenides is the low ionization potential organometallic sandwich compounds--

metallocenes¹⁶⁻¹⁸, bis(arene)metal compounds^{17,18}, and some mixed sandwich compounds¹⁷. The sandwich compounds are thought to act as pseudo-alkali metals in intercalation. The organometallic sandwich compound intercalates offer another opportunity and avenue of approach to gauge the relative importance of guest-guest and guest-host interactions to the structure and bonding in layered transition metal dichalcogenide intercalation complexes and the possibility of reagents with usefully modified reactivity.

The recent report by Chianelli and Dines¹⁹ of low-temperature preparations of Group IV B, V B, and VI B dichalcogenides by solution metathesis reactions offers a route to several forms of layered dichalcogenides not available by the traditional high-temperature elemental syntheses¹. The compounds formed in these low-temperature solution syntheses show reactivities, particularly toward intercalation, not previously accessible.

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REACTIVITY OF POLYSTYRENE-BOUND BIPYRIDINE AND THE CATALYTIC POTENTIAL OF ITS TRANSITION METAL COMPLEXES

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Since 1971, there has been a growing interest in catalysis by solid supported transition metal complexes.¹ The metal complex which is grafted onto a support can either be an established homogeneous catalyst or its metal center could acquire catalytic activity after the process of heterogenization.

Crosslinked polystyrene is a commonly used solid support and numerous ligands have been anchored to this resin through covalent bonds. The resin which is functionalized with the analog of tri-phenylphosphine²⁻⁴ is known to heterogenize potent homogeneous catalysts. However it has the following drawbacks: 1, air sensitivity of the phosphorus center; 2, lability of phosphine-metal linkage in some systems; 3, polymer crosslinking induced by the complex which modifies the primary structure of the support.

In order to bypass the above disadvantages, we have independently undertaken a study of the reactivity of a polymer bound bipyridine [(P)-Bipy] reported by Neckers et al.⁵ and investigated the catalytic activity of some of its transition metal complexes towards hydrogenation. The choice of immobilized bipyridine stems from the fact that this ligand stabilizes a wide range of metal oxidation states and functions as a chelate.

The bonding properties of (P)-Bipy were studied by reacting it with a series of carbonyl containing metal complexes and then comparing the IR spectra (C-O stretching region) of the various polymer attached products with those of compounds derived when bipyridine undergoes the corresponding reactions. Polymer bound pyridine was used in similar reactions to ascertain the bidentate behavior of (P)-Bipy. Thus, (P)-Bipy was reacted with Mo(CO)_6 , $(\text{CO})_2\text{RhCl}/2$, and $(\text{CO})(\text{PPh}_3)\text{RhCl}/2$ to form (P)-Bipy Mo(CO)_4 , [(P)-Bipy $\text{Rh(CO)}_2\text{Cl}$, (P)-Bipy RhCOCl] and (P)-Bipy $\text{Rh(PPh}_3\text{)Cl}$ respectively. The further reaction of (P)-Bipy Mo(CO)_4 with PPh_3 generated (P)-Bipy $\text{Mo(CO)}_3(\text{PPh}_3)$. These investigations indicate that (P)-Bipy functions as a bidentate ligand.

Catalytic hydrogenations were observed with the following catalyst precursors: (P)-Bipy PtCl_2 , (P)-Bipy PdCl_2 , polystyrene dispersed palladium metal and (P)-Bipy $\text{Rh(PPh}_3\text{)Cl}$. The system (P)-Bipy PtCl_2 shows a high degree of selectivity towards the hydrogenation of terminal olefinic bonds. The material (P)-Bipy PdCl_2 reduces a wide variety of coordinating and non-coordinating substrates (with isomerization where applicable) and polymerizes methyl acrylate. The activity of this catalyst can be attributed in part to the presence of metallic palladium. Polystyrene dispersed palladium was found to be a factor of 2-3 times slower (rate of H_2 uptake) than 5% Pd/C in hydrogenating p-benzoquinone and nitrobenzene. This system (P)-Bipy $\text{Rh(PPh}_3\text{)Cl}$

is even more effective in hydrogenating internal and terminal double bonds than (P)-BipyPdCl₂. Tentative mechanisms are discussed for the activity of both (P)-BipyPtCl₂ and (P)-BipyRh(PPh₃)Cl. All of the above catalyst precursors have been reused without any loss of activity.

In summary, the use of immobilized bipyridine has facilitated the understanding of the coordination sphere of the grafted metal complex and generated some novel hydrogenation catalysts.

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Synthesis and Stereodynamics of Tetrairidiumdodecacarbonyl

Derivatives

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(Final Seminar)

May 16, 1978

It has been proposed that transition metal cluster compounds may serve as models of a heterogeneous surface.¹ The mobility of coordinated carbon monoxide and the C-H bond scission of organic compounds are two processes common to both metal clusters and metal surfaces which are of current interest.

New synthetic techniques have been developed for the preparation of iridium carbonyl cluster compounds. Reductive carbonylation of the readily available Ir(I) species $\text{Ir}(\text{CO})_2(\text{p-toluidine})\text{Cl}$ under moderate conditions (5 atm CO, 90°C) provides $\text{Ir}_4(\text{CO})_{12}$ in high yield.² The addition of one-fourth equivalent of a phosphorus ligand to the reaction mixture allows the direct preparation of mono- and di-phosphorus ligand derivatives of $\text{Ir}_4(\text{CO})_{12}$.³ Furthermore, it was found that the replacement of carbonyls in $\text{Ir}_4(\text{CO})_{12}$ by a wide variety of ligands can be facilitated through the use of $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ as an oxidative decarbonylation reagent. In this manner complete series of $\text{Ir}_4(\text{CO})_{12}$ derivatives, having up to four carbonyls replaced, have been prepared for a number of isonitrile and phosphorus ligands.

NMR (^{13}C , ^{31}P , ^1H) studies have shown that the phosphorus ligand derivatives adopt structures with three bridging carbonyl ligands.⁴ In contrast, the isonitrile derivatives generally adopt structures with only terminal carbonyls. Variable temperature ^{13}C NMR studies indicate that carbonyl site exchange in the mono-substituted derivatives occurs by rapid interconversions between carbonyl bridged and unbridged structures⁴ as originally proposed by Cotton for $\text{Rh}_4(\text{CO})_{12}$ and $\text{Co}_4(\text{CO})_{12}$.⁵

The direct reaction of $\text{Ir}_4(\text{CO})_{12}$ with 1,5-cyclooctadiene resulted in products arising from partial dehydrogenation of the organic ligands. Subsequent crystal structure determinations (Dr. C. G. Pierpont) revealed several unusual bonding modes for the organic moieties in two of these complexes. In $\text{Ir}_7(\text{CO})_{12}(\text{C}_8\text{H}_{12})(\text{C}_8\text{H}_{11})(\text{C}_8\text{H}_{10})$ the C_8H_{11} ligand is bound to an edge as a vinyl moiety by one σ and one π bond. The C_8H_{10} ligand bridges one triangular face and is bound with two σ and one π bond.⁶ In contrast, the C_8H_{10} unit in $\text{Ir}_4(\text{CO})_5(\text{C}_8\text{H}_{12})_2(\text{C}_8\text{H}_{10})$ was found to be inserted into an Ir-Ir bond to give a Ir_4C_2 pseudo-octahedral cluster framework.⁷ Several simple 1,5-cyclooctadiene derivatives of $\text{Ir}_4(\text{CO})_{12}$, ($\text{Ir}_4(\text{CO})_{12-2x}(\text{C}_8\text{H}_{12})_x$, $x=1-3$) were prepared under milder conditions and the intermediacy of these compounds in the formation of $\text{Ir}_4(\text{CO})_5(\text{C}_8\text{H}_{12})_2(\text{C}_8\text{H}_{10})$ was established. The results imply that the formation of $\text{Ir}_4(\text{CO})_5(\text{C}_8\text{H}_{12})_2(\text{C}_8\text{H}_{10})$ involves two sequential oxidative additions of olefinic C-H bonds, followed by the insertion of the resultant acetylenic unit into an Ir-Ir bond giving the Ir_4C_2 pseudo-octahedral framework.⁷

The mechanisms of carbonyl mobility and C-H bond scission determined for these iridium clusters provide models for related processes which occur on metal surfaces.

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INCLUSION BY MOLECULAR CAVITIES: APPLICATIONS

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October 12, 1978

The flexibility offered by the use of molecular cavities has excited much interest in spite of the added complications involved with their application. Zeolites,¹ silicates,² and graphite³ represent long-standing examples of exploitation of cavities for various applications. The quest for solution phase cavities is satisfied, at least in part, with cyclodextrins,^{4,5} sugar derivatives, and cryptands,^{6,7} synthetic multicyclic heteroatom compounds. The purpose of this seminar is to review some properties and selected examples of the use of molecular cavities, some of which are large enough to contain substituted aromatics and others which can only include small molecules and metal ions.

SMALL CAVITIES

Most of the research with cryptands has dealt with the bicyclic compounds such as $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N$ denoted as [2.2.2], although other topologically different derivatives are known. Early research showed that [2.2.2] prefers to include the potassium cation while [3.3.2] exhibited nearly equal formation constants for potassium and rubidium cations. The observed stability was described in terms of the number and type of binding sites leading to the "cryptate effect" while the selectivity was seen to be a function of the fit of cavity size with the metal cation size.⁸ The temperature dependence of the complex formation showed that the change in enthalpy reflected the selectivity of a particular cryptand.⁹ In methanol, both selectivity and stability of the included complexes were enhanced.^{8,9} It was observed that, in methanol, the alkaline-earth complex with the greatest stability also possessed the greatest activation enthalpy for dissociation.¹⁰ Similar characteristics were also observed with alkali cations¹¹ and it was suggested that the transition state for formation of the complex closely resembles the state of the reactants.^{10,11} The energy of desolvation of the metal cation would be compensated by interaction with the complex.

Recent applications of small cavities have included the preparation of inert lanthanide cryptates,¹² stabilization of the sodium anion,^{13,14} and use in forming isolated counter-ions.¹⁵

LARGE CAVITIES

A convenient source of large cavities is provided by the cyclodextrins which are α -1,4-linked cyclic oligomers of D-glucopyranose (α , β , and γ refer to 6, 7 and 8 glucose units, respectively) which form a hollow, hydrophobic, truncated cone ringed by twelve secondary hydroxyl functions at the large end, and six primary hydroxyl functions at the other end.¹⁶ A wide variety of molecules can be included into cyclodextrins resulting in many suggestions for the driving force for inclusion. Nuclear magnetic resonance¹⁷ and crystal structure determinations¹⁸ have been employed to examine the nature of the binding and orientation of included benzoic acid and sodium benzoate. These studies have

shown that in both cases the acid function is located inside the cavity. A comprehensive model of the thermodynamics of inclusion of aquated apolar substrates was recently reported.¹⁹

The applications of cyclodextrins have been numerous: the resolution of chiral sulfinyl compounds,²⁰ the preparation of Vitamins K₁ and K₂,²¹ and catalytic hydrolysis of amides.²² Furthermore, the substrate binding by enzymes can be modeled with cyclodextrins or derivatives.^{23,24}

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Intervalence Electron Transfer in Mixed Valence Compounds

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Final Seminar

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Experiments aimed at understanding the energetics and rates of intervalence electron transfer in a variety of mixed-valence compounds have been undertaken to try to obtain a data base for testing current theories regarding more general electron transfer phenomena. These theories can be applied in areas of chemistry and physics ranging from electrochemistry to semiconductor science. In particular, an attempt has been made to check the validity and/or the limitations of the Hush theory¹, which relates the energy of the intervalence transfer band observed in the electronic spectrum to the energy of the thermal barrier to intervalence electron transfer within the mixed-valence compound.

Part of the research effort has been directed at studying mixed-valence compounds which show behavior which might be indicative of a breakdown in the Hush theory. One such compound is the mixed-valence [2,3] oxidation state of the dimer μ -pyrazine-bis(pentaammineruthenium) tosylate, which contains one Ru(II) and one Ru(III). Since Creutz and Taube² first reported the synthesis of this dimer in 1969, it has been the subject of a great deal of interest and controversy in the literature. It exhibits an intervalence transfer band which has neither the band width nor the solvent dependence predicted on the basis of the Hush theory. The many attempts which have been reported to experimentally determine the rate of intervalence electron transfer have led to ambiguous results.

To further our understanding of this compound and the Hush theory, we conducted experiments³ to help us formulate a description for the molecular orbitals involved in the electron transfer and to determine the rate of intervalence electron transfer between the two metal centers. Variable temperature magnetic susceptibility results on the [3,3] pyr dimer coupled with low temperature EPR results for both the [2,3] pyr and [3,3] pyr dimers indicate that the odd electron in the dimer resides in the (d_{xz}, d_{yz}) orbital set on the Ru(II) center and is not in a molecular orbital which is delocalized over both metals as postulated by Hush⁴. Variable temperature studies

indicate that in solution the rate of electron transfer from the Ru(II) center to the Ru(III) center is fast on the NMR time scale of 10^{-5} sec from room temperature down to -80°C . It is slow on the EPR time scale of 10^{-9} sec in the solid state at all temperatures below -50°C . If outer coordination sphere effects are assumed to be negligible, then these EPR and NMR results can be used to bracket the magnitude of the thermal energy barrier to between 3.4 and 6.7 kcal/mole. This is in agreement with the Hush theory prediction of 4.5 kcal/mole, which is based on the energy of the IT band. However, it may be that in the solid state, outer coordination sphere effects dominate, and that lattice effects can lock the odd electron onto one valence site.

The other part of this research effort concerning mixed-valence compounds has been focused on trying to develop better experimental techniques for studying the intervalence electron transfer phenomenon. The technique which has been investigated most extensively is time domain reflectometry, or TDR^{5,6}. This technique can be used to study the dielectric relaxation properties of samples in the frequency range from 10^6 Hz up to 10^{10} Hz. The charge oscillations associated with intervalence electron transfer can give rise to such dielectric relaxation. Analysis of TDR data can yield the relaxation frequency associated with the relaxation process, which can be used to calculate the rate of electron transfer. Variable temperature TDR data can be used to calculate the magnitude of the thermal energy barrier to electron transfer by using the Arrhenius equation.

TDR data has been obtained for a sample of europium sulfide which analyzes as Eu_4S_5 . Analysis of the data indicates that the rate of electron transfer in this mixed valence compound is $2.2 \times 10^9 \text{ sec}^{-1}$ at room temperature, and that the magnitude of the thermal energy barrier to the electron transfer process is around 920 cal/mole. This barrier corresponds almost exactly to the band gap energy associated with the semiconductivity of the compound. This has been determined from IR measurements, where the edge of the band gap absorption feature can be observed at around 320 cm^{-1} . These results represent the first reported use of time domain reflectometry on solid samples, and the first time the technique has been used to

determine the rate of electron transfer in a mixed valence compound.

Other mixed-valence compounds have also been studied. Magnetite, or Fe_3O_4 , exhibits a rapid relaxation process which appears to be fast on the TDR time scale. This result is consistent with Mossbauer results which have been obtained for the compound⁷. Soluble Prussian blue exhibits a relaxation process which is observable in the TDR, but is slow on the TDR time scale of 10^{-6} sec, which also agrees with the Mossbauer results⁸. No relaxation is observed for solid $\left[\left((\text{NH}_3)_5\text{Ru} \right)_2\text{pyr} \right]^{5+}$ tosylate. This is consistent with the EPR study³ which indicates that the odd electron in the dimer is localized on one metal center in the solid state. The mixed-valence trimer $\text{Fe}^{2+}\text{Fe}_2^{3+} \text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_5$, reported by Gol'danskii⁹ to exhibit dynamic electron transfer on the Mossbauer time scale, has also been studied. It does not exhibit the expected dielectric relaxation in the TDR, nor do several other mixed-valence oligamers which have been studied. It is currently not known whether this means that the TDR technique is only sensitive to electron transfer in extended lattice systems, or that literature estimates of electron transfer rates are incorrect for these systems.

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PHOTO-OXIDATION OF INORGANIC COMPOUNDS
WITH APPLICATION TO SOLAR ENERGY

Richard W. Wegman

October 26, 1978

Thermal conversion and quantum conversion are two fundamental ways for converting solar energy into useful energy. A thermal system utilizes a collector that transforms light energy into heat.¹ The heat is transferred to a thermal storage system for use at a later time. Quantum conversion utilizes the available solar energy to induce a photochemical or photoelectric process in the absorbing material. In a photochemical process the absorber is activated to an excited state by the absorption of light. The energy gained by the absorber is lost by deactivation of the excited state through radiative and non-radiative decay processes.² An energy storage system coupled to the excited state provides an alternative deactivation pathway by directing the excess energy into a process that produces a stable fuel.³ The efficiency of the energy storage process is limited by certain thermodynamic and kinetic parameters of the absorbing system. The thermodynamic limitations include:

- 1) The maximum chemical potential difference achievable between the ground and excited state;⁴ and
- 2) Power drainage into the storage system and its effect on the photo-generated chemical potential.⁵

The kinetic limitations arise from the inherent microreversibility of the system.⁶

The photo-dissociation of water into O_2 and H_2 is a very attractive system for solar energy conversion.⁷ Hydrogen is an excellent fuel and the source is cheap and plentiful. Unfortunately, high energy photons, not abundant in solar radiation, are required for direct photo-decomposition of water. Chemical systems that photo-catalytically decompose water by utilizing lower energy photons are therefore necessary. One of the oldest known systems involves the photo-oxidation of $Ce(III)$ to $Ce(IV)$ in dilute perchloric acid solution.⁸ The process begins with the photo-excitation of $Ce(III)$ to $*Ce(III)$. The $*Ce(III)$ ion reduces H^+ resulting in the production of H_2 gas and $Ce(IV)$. The system is cyclic because $Ce(IV)$ is capable of oxidizing water to regenerate H^+ and $Ce(III)$.

A similar system involves the photo-oxidation of $Cu(I)$ to $Cu(II)$ in the presence of H^+ .⁹ This process is non-cyclic because $Cu(II)$ cannot oxidize water to regenerate starting materials. A mechanism for H_2 production in this system has recently been proposed.¹⁰

The photo-excitation of $Ru(bpy)_2^{2+}$ to $*Ru(bpy)_2^{2+}$ and the consequent reduction of water by $*Ru(bpy)_2^{2+}$ has been suggested as a plausible method for water decomposition.¹¹ Apparently, for kinetic reasons, the electron transfer process is too slow to compete with excited state decay. Recently, Meyer¹² has reported a working

photo-electrochemical cell utilizing $\text{Ru}(\text{bpy})_3^{2+}$. The cathode is a solution containing $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ in 1 N H_2SO_4 . The anode is a solution containing $\text{Fe}(\text{II})$ and $\text{Fe}(\text{III})_2^{3+}$ also in 1 N H_2SO_4 . Photolysis of the cathode produces $^*\text{Ru}(\text{bpy})_3$ which is oxidized by $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ to give $\text{Ru}(\text{bpy})_3^{3+}$. A current is produced by the oxidation of $\text{Fe}(\text{II})$ by $\text{Ru}(\text{bpy})_3^{3+}$.

The photochemistry of di-nuclear metal complexes is of current interest and recently a rhodium¹³ and several molybdenum di-nuclear compounds^{14,15} have been shown to stoichiometrically reduce H^+ to H_2 during photolysis.

The systems developed thus far have inherent problems which render them inadequate for the practical production of fuels. These problems include:

- 1) High energy excitation wavelengths;
- 2) Low quantum yields in the conversion process;
- 3) Non-cyclic systems.

Research oriented towards the engineering of systems capable of working at a practical level is necessary.

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LIGAND EXCHANGE STUDIES OF METHYLCOBALAMIN AND
MODEL METHYLATOCOBALT(III) CHELATE SYSTEMS

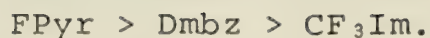
Pamela Milton

December 5, 1978

Alkylatocobalt(III) chelate systems, containing planar or nearly planar ring systems, have been extensively investigated as models for alkylcorrinoid systems. Although a considerable amount of equilibrium data exists for base substitutions and exchanges of alkylcorrinoid systems, the only kinetic study of methylcobalamin thus far reported involves a spectrophotometric investigation of the cyanation reaction of methylcobalamin in alkaline medium.¹ The value of 0.028 sec^{-1} derived as the rate constant at 25°C for displacement of dimethylbenzimidazole (Dmbz) by cyanide in methylcobalamin¹ is inconsistent with the observation of fast exchange in the ^1H and ^{13}C NMR spectra of methylcobalamin at room temperature.^{2,3}

By protonation of methylcobalamin to the half-equivalence point and utilization of methanol as solvent, NMR spectra were obtained in the intermediate and stopped exchange region for Dmbz dissociation from methylcobalamin. Activation parameters for the dissociation of Dmbz from methylcobalamin were determined from detailed fitting of ^{13}C and ^1H NMR line shapes in the $\text{CH}_3\text{-Co}$ region. An Arrhenius plot based on the combined data, which were in good agreement, yielded $\Delta H^\ddagger = 11.1 \pm 0.6 \text{ kcal/mol}$, $\Delta G^\ddagger = 12.7 \pm 0.1 \text{ kcal/mol}$, and $\Delta S^\ddagger = -5.9 \pm 2.4 \text{ cal/(K mol)}$. The rate of Dmbz dissociation in 50% methanol-water was found to be essentially the same as in neat methanol. The ΔH^\ddagger for Dmbz dissociation is significantly lower than expected, based on comparison with ΔH^\ddagger for dissociation of 1-(2-trifluoromethylphenyl)imidazole (CF_3Im) from the methyl derivative of heptamethyl ester of cob(III)yrinic acid (methylcobester).⁴ This lower value may be ascribed to repulsive steric interactions which hinder the approach of Dmbz to cobalt.

In an attempt to establish a firmer basis for comparing the interaction of CF_3Im and Dmbz with differing cobalt centers, the kinetics of Dmbz dissociation from methylcobaloxime was examined. Activation parameters for CF_3Im dissociation from methylcobaloxime have been reported previously by Guschl and Brown.⁴ The axial coordination site of methylcobaloxime should be much less hindered sterically than that of methylcobalamin. Two sets of variable temperature NMR data were collected for solutions containing equimolar Dmbz and benzonitrile adducts with methylcobaloxime in nitrobenzene. Unfortunately, rather large uncertainties are associated with the values of ΔH^\ddagger and ΔS^\ddagger calculated for Dmbz dissociation from methylcobaloxime due to the rather limited temperature range available for study. Thus, no firm conclusions can be made for this system with regards to differences in activation enthalpies for Dmbz and CF_3Im exchange with methylcobaloxime. However, relative values of ΔG^\ddagger and rate constants, obtained in this study and a previous study⁴, indicate that the labilities of several heterocyclic base complexes with MeCbx decrease in the order:



An investigation of ligand exchange reactions of methylcobester was undertaken in an effort to obtain comparative kinetics information for the interaction of bases with methylcorrinoid complexes in nonpolar, non-interacting solvents. Establishment of NMR two-site exchange systems for methylcobester derivatives proved to be difficult. Only for the case of CF_3Im adduct was the slow exchange region clearly established. It was possible, nonetheless, to extract valuable information from the base concentration dependence and temperature dependence of the NMR spectra of various derivatives, such as benzimidazole, 3-fluoropyridine, and CF_3Im . Implications of these studies with regards to cobalamin binding to proteins and enzymes and its coenzyme activity will be discussed.

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NITROGEN-14 NUCLEAR QUADRUPOLE RESONANCE SPECTRA OF COORDINATED PYRIDINE

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The number and variety of ^{14}N NQR data available for compounds in which a nitrogen atom is coordinated directly to a metal ion or other Lewis acid is quite limited. Difficulties in the measurement of low frequency (3 to 0.2 MHz) ^{14}N resonances for coordinated nitrogen are avoided by using an adiabatic demagnetization in the laboratory frame double resonance experiment.¹ By this method, the protons in a sample are first allowed to approach equilibrium alignment in a high magnetic field; next, the same is removed to zero field, where it is irradiated at a known frequency and subsequently returned to high field where a wide line NMR experiment determines the magnitude of the proton magnetization. Should the zero field irradiation frequency approach a ^{14}N quadrupole resonance line, energy is resonantly absorbed by the nitrogen nuclei. Some of this energy is transferred to the proton system by level crossing, which in turn reduces the proton magnetization relative to that obtained when no energy is absorbed by the nitrogen nuclei. By repeating this cycle, a spectrum of irradiation frequency versus proton magnetization exhibits peaks corresponding to the ^{14}N resonances.

Nitrogen-14 NQR data for pyridine-Lewis acid complexes have been obtained and interpreted in terms of nitrogen orbital occupancies using a modified Townes-Dailey model.² For each quadrupole coupling constant and assymetry parameter obtained for pyridine nitrogens, a donor orbital population, $\sigma_{\text{D.O.}}$, can be calculated. It is assumed that the nitrogen is sp^2 hybridized when coordinated, and that the π and N-C σ orbital populations are given by:

$$a = a_o + A(2 - \sigma_{\text{D.O.}})$$

$$b = b_o + B(2 - \sigma_{\text{D.O.}})$$

respectively, where a_o and b_o are the respective free ligand populations, and A and B are constants calculated from the NQR data. That is, the populations of the π and N-C σ orbitals are allowed to increase in proportion to the loss of electron density from the lone pair orbital.

Pyridine complexes with lithium, zinc(II), cadmium(II), mercury(II), silver(I) and iron(0), pyridine-halogen compounds and pyridinium salts among other Lewis acid centers are discussed in terms of the effect of coordination on the nitrogen donor orbital of pyridine. Correlations of this donor orbital population with infrared absorption bands, nitrogen-acid bond lengths and halogen NQR are also described.

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KINETIC ISOTOPE EFFECTS OF OXIDATIVE ADDITION OF HYDROGEN TO METAL COMPLEXES

David J. Blumer

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Introduction

Since the discovery of the oxidative addition reaction of H_2 , O_2 , CH_3I , and many other species to transition metal complexes,¹ much effort has focused on determining whether this is an analogous reaction to the chemisorption of a gas on a metal surface. As more refinements of work from both sides of the problem with respect to both surface processes and homogeneous catalysis come to light, certain similarities seem to prevail.²

In 1965, Chock and Halpern³ measured the kinetics of the oxidative addition of H_2 , O_2 , and CH_3I to $trans-Ir(CO)Cl(P(C_6H_5)_3)_2$. They also reported a kinetic isotope effect of 1.22 at 30°C for the ratio of the rate of addition of H_2 to the addition of D_2 . The present work was aimed at a systematic study of the kinetic isotope effect of this reaction as a prototype of catalytic activation of H_2 , as well as development of more sophisticated experimental methods and theoretical analysis.

Theory

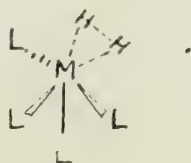
Theoretically, the kinetic isotope effect can be described within the transition state theory as the ratio of statistical mechanical partition function for each of the isotopic species. This is commonly broken down into the product of the mass-moment of inertia (MMI), the excitation term (EXC), and the zero-point energy (ZPE) terms. In organic chemistry, it is common (and usually accurate) to ignore the MMI and EXC terms since they are nearly 1.0. In inorganic reactions, this may be very dangerous, as will be pointed out. In general, simplistic arguments concerning the amount of bond-breaking and bond-making in the transition state for inorganic reactions should be viewed with scepticism, since this study has shown that even state-of-the-art theoretical calculations cannot make such concrete statements.

Calculations

Computer calculations were undertaken to explore the effects of having three vibrational modes contributing to the reaction coordinate, the effects of quantum-mechanical tunnelling, the temperature dependence, the transition state geometry, and the transition state force field on the kinetic isotope effect.⁴ Many models of the transition state were investigated, ranging from a simple three-atom system, $H---H$, to more

M

complex models such as



Apparatus

In order to measure the kinetic isotope effect, an apparatus was designed and constructed which can measure the rate of uptake or release of a gas in a reaction very accurately. The system is automated with the time and pressure data recorded on a cassette tape, which is read into a PDP-11 computer for kinetics analysis and display. The rate of reaction with each isotopic gas was measured and then the ratios of the rates taken to obtain the kinetic isotope effect.

Results and Conclusions

The kinetic isotope effect of the oxidative addition of hydrogen to $\text{Ir}(\text{CO})\text{Cl}(\text{P}(\text{C}_6\text{H}_5)_3)_2$ in toluene was temperature dependent and ranged from 1.05 to 1.33 at 26.77°C and 50.0°C, respectively. This was interpreted in terms of the transition state properties, which must include a hindered rotation of the H---H moiety and two bending vibrations of the triangular M-H₂ group, in addition to the contributions mentioned above.

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SUPER-IONIC CONDUCTIVITY IN NON-STOICHIOMETRIC OXIDES

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February 15, 1979

Introduction

Interest in solids with ion conducting properties has increased due to their potential use as solid electrolytes and as electrodes in energy conversion systems. Ionic conductivity arises as the result of imperfections in a crystal structure. Transportation of ions occurs by interchange between normal sites and defect sites in the crystal lattice. Frenkel and Schottky defects are intrinsic lattice defects and will be present in any pure ionic crystal above 0 K. Statistical thermodynamics shows that in NaCl, at room temperature, there are on the average one defect for each 10^6 ions [1-4].

A defect can also be caused by the presence of a foreign ion in a normal lattice site. If the impurity has a different charge, the production of a vacancy is required to keep electrical neutrality within the crystal. Non-stoichiometry can result if either an excess of cations or an excess of anions is present. Beta-alumina, an example with mobile cations, is a sodium conductor used in Na/S batteries. Calcia stabilized zirconia, an example with mobile anions, is an oxygen conductor for hydrocarbon-air fuel cells and for oxygen concentration electrodes.

Beta-Alumina

An idealized crystal structure was determined in 1937 by Beevers and Ross to have the formula $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$. The crystal is composed of spinel blocks bound together by loosely packed layers containing Na^+ and O^{2-} ions [5]. The crystal structure was refined in 1971 and found to have approximately 29% excess sodium in the conduction band and a formula of $\text{Na}_{1+x}\text{Al}_{11-x/3}\text{O}_{17}$, such that $0.15 < x < 0.30$ [6].

It was found that sodium could be exchanged for other cations in the beta-alumina structure. Ion exchange is preformed at 300°-350°C from the molten nitrate salt. Tracer diffusion experiments were carried out to determine the ionic conductivity of the various cations. The fact that Na^+ beta-alumina exhibits the highest conductivity probably indicates that it is the ideal size conductor [7].

Techniques done to study the ionic conduction band in beta-aluminas include: x-ray diffraction [5,6], neutron diffraction [8], nuclear magnetic resonance [9], infrared and raman spectroscopy [10,11], and electron paramagnetic resonance [12]. The general consensus is that at elevated temperatures the conducting cation is not localized in a specific lattice site but moves through the lattice with a disorder pattern which resembles that of a two-dimensional liquid.

In recent years beta-alumina has been developed into an electrolyte for use in a sodium sulfur battery [13]. One cell designed by the Ford Motor Co. was operated for over two years and was fully recharged in excess of 9800 times.

Calcium Stabilized Zirconium Oxide

At elevated temperature and when doped with 10% to 20% calcium oxide, zirconium oxide forms in the fluorite crystal structure and shows abnormally high oxygen ion conductivity. The Ca^{+2} ion replaces the Zr^{+4} ion in the crystal and electrical neutrality requirements cause the creation of an oxygen anion vacancy [14]. Because this structure has so many 'holes' in the crystal lattice, rapid ionic diffusion is expected.

Various aspects of ionic conduction have been studied. These include effects of composition, temperature, as well as oxygen pressure on the oxygen ion conductivity. It was found for $(\text{CaO})_{0.15}(\text{ZrO}_2)_{0.85}$ that the calcia concentration at maximum conductivity increased from about 13 mol% at 1000°C to about 15 mol% at 1400°C [15].

Calcium stabilized zirconia electrolytes have been used in many different ways in recent years. It has found use in high temperature fuel cells due to its noncorrosive, as well as chemical, thermal and mechanical stability properties [16]. It has also found a place in electrodes used to measure the oxygen concentration in both high-temperature gases and liquid metals [17,18].

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POLYOXOANION CHEMISTRY

Peter Dimas

February 20, 1979

Occurrence and Structure

A prominent feature of the aqueous chemistry of molybdate, tungstate and vanadate ions is their polymerization upon acidification to form large polyoxometallate anions [1]. The basic building unit of these anions is an octahedron of six oxygens surrounding each metal atom. Clusters of these octahedra are linked by sharing apices, edges, or, less often, faces [2]. Polyoxoanions which contain only oxygen, the metallate atom, and possibly hydrogen, are termed isopoly ions. Heteropoly ions are those structures in which a heteroatom or various functional groups have been incorporated [3].

Current Research Motivation

Much current interest in polyoxoanions is motivated by their diverse applications as heterogeneous catalysts [3]. Furthermore, polyoxoanions resemble fragments of close-packed oxide lattices and the behavior and properties of such anions may be used as a model for metal oxide catalyst-substrate interactions [4,5].

A clear understanding of the solution dynamics and transformations of polyoxoanions is being sought in order to determine the mechanistic principles governing formation and reactivity of various polyoxoanions [6], and to develop useful homogeneous catalysts.

Also of interest is the ability of polyoxoanions to undergo facile, multi electron reduction to isostructural, Class II mixed-valence species which are called 'heteropoly blues' in recognition of their strong absorption in the red region of the visible spectrum [2].

Polymerization Mechanisms [6]

Two fundamental constructional principles, the addition and condensation mechanisms, have been proposed. These mechanisms account satisfactorily for the particular species formed as well as for the rapid rates of formation observed.

Dynamic Solution Behavior

Investigation of two hexamolybdoorganoarsonates [7], $(\text{PhAs})_2\text{Mo}_6\text{O}_{24}^{4-}$ (A), and $(\text{PhAs})_2\text{Mo}_6\text{O}_{25}\text{H}_2^{4-}$ (B), has shown them to differ by a constitutional water molecule. Rapid solution

interconversion of the edge-linked A form to B, which contains a shared face, proceeds by insertion of a bridging water into the A structure in wet or aqueous solutions. Similar fluxional behavior is observed for the corresponding tungstate, but must be induced by protonation [8]. These systems suggest the importance of face-sharing in polyoxoanion hydrolyses.

The dynamic stereochemistry of $\alpha\text{-Mo}_8\text{O}_{26}^{4-}$ has been investigated by ^{17}O FT-NMR [9]. The two tetrahedral molybdate subunits are found to reorient rapidly within the structure, either inter- or intramolecularly. A simple relationship between kinetic lability and low bond order is established and its implications concerning reactivity of other polyoxoanions are discussed. An exchange experiment between $\text{M}^{18}\text{O}_4^{2-}$ and $\alpha\text{-Mo}_8\text{O}_{26}^{4-}$ might indicate whether the reorientation process is inter- or intramolecular.

The facile interconversion of two $\text{Mo}_8\text{O}_{26}^{4-}$ isomers has been discovered [10]. An intramolecular rearrangement process has been suggested but experimental verification is required.

The decomposition equilibrium between the labile $\text{Mo}_5\text{O}_{17}\text{H}^{3-}$ anion to the products $\alpha\text{-Mo}_8\text{O}_{26}^{4-}$ and $\text{Mo}_2\text{O}_7^{2-}$ has been elucidated by IR [11]. The weakly bound MO_4^{2-} unit and proton account for the observed lability. A mechanism has been proposed.

The rate of ^{18}O exchange between H_2O and $\text{V}_{10}\text{O}_{28}^{6-}$ has been investigated [12]. A mechanism involving partial fragmentation of the anion has been developed to explain the observed exchange equivalency of all twenty-eight oxygen atoms.

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ASYMMETRIC HYDROGENATION USING WILKINSON-LIKE CATALYSTS

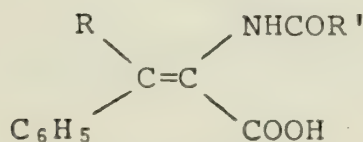
Sharon A. Brawner

February 27, 1979

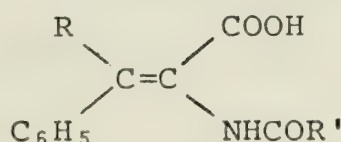
The synthesis of optically active compounds with high optical purity is a challenging problem. A common route in the preparation of optically active compounds is the reaction of a chiral reactant with a prochiral substance [1]. Despite high optical yields, a major disadvantage of this method is the necessity for stoichiometric quantities of chiral reactants. Therefore it is desirable to prepare an asymmetric catalyst which can produce chiral compounds of high optical purity without the use of chiral reactants. Heterogeneous techniques, which generally lacked stereospecificity, resulted in low optical yields and irreproducible results [2]. Stimulated by the development of Wilkinson's catalyst [3] and synthetic routes to optically active phosphines [4], homogeneous catalysis has received much attention, in an attempt to optimize optical yields. One of the most effective asymmetric catalyst systems has been developed by generating the active species in situ from $[\text{Rh}(\text{diene})\text{L}_n]^+\text{X}^-$ where L is an optically active phosphine.

In the design of an efficient asymmetric catalyst the choice of ligand is crucial. Using a ligand chiral at phosphorus, Knowles was able to obtain modest optical yields in the hydrogenation of α - β -unsaturated carboxylic acids [5]. Attempts to improve optical yields were successful by modification of the phosphine with bulky substituents. Morrison [7] and Kagan [8] also obtained good asymmetric induction in the hydrogenation of α -acylaminoacrylic acids, using ligands in which the chirality resided on an aryl or alkyl substituent of the phosphine and a chelating diphosphine, respectively.

The nature of the substrate is also important in achieving high optical yields. Excellent results have been obtained in the hydrogenation of α -acylaminoacrylic acids. This has been attributed to their tridentate structure with coordination to rhodium occurring through the olefin, amide and carbonyl functional groups [9]. Another factor found to influence optical yield was the E or Z geometry of the olefin, the Z isomer being reduced with higher stereoselectivities and higher rates of hydrogenation [9, 10].



(E)-isomer



(Z)-isomer

Geometric isomers of α -acylaminoacrylic acids

Although there has been a great deal of research involving asymmetric hydrogenation, little has been done to elucidate a detailed reaction mechanism. ^{31}P , ^1H NMR and kinetic studies were conducted by Brown [11] and Halpern [12] on rhodium catalysts with chelating diphosphine ligands. The results were indicative of a mechanism in which the stereochemical course of the reaction is defined by olefin coordination to rhodium followed by oxidative-addition of hydrogen. ^{31}P NMR studies of rhodium catalysts with monophosphine ligands suggest that the primary reaction pathway in hydrogenation is dependent upon the structure of the phosphine [13].

The dependence of optical yield upon E or Z geometry of the olefin was examined by deuteration studies and ^1H NMR [14, 15]. E \rightarrow Z isomerization was found to be responsible for this dependence. Although addition-elimination is the major mechanistic pathway for the isomerization of olefins, catalyzed by Rh(III) species [16], both Knowles [15] and Kagan [14] have rejected this pathway. For the catalyst $[\text{Rh}(\text{DIOF})\text{S}]^+$ Kagan proposes pathways involving orthometalation of a phenyl ring on the substrate or the formation of an immonium intermediate [14]. For $[\text{RhL}_n\text{S}]^+$ where L is a variety of mono- and diphosphines, Knowles postulates a π -allyl mechanism to account for the observed isomerization [15].

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FERROFLUIDS

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March 27, 1979

A ferrofluid is a colloidal suspension of magnetic particles in a liquid. The particles are stabilized by surfactant molecules adsorbed on the surface of the particles which are solvated by the carrier liquid [1]. The presence of a magnetic field does not separate the two phases, but causes the liquid to move with the particles as if the fluid were homogeneous.

Ferrofluids were originally designed as a means of controlling fuel flow under the zero gravity conditions of free space. The fluids became commercially available in the early 1970's. Applications of the fluids cover a wide range of areas; use in loudspeakers, zero-leakage seals, damping liquids, magnetic ink, nonwearing electrical switches, artificial muscle [2], ore separation [3, 4], and energy converters [5].

The magnetic particles in the fluid are single domain ferromagnets, which exhibit paramagnetic behavior. This phenomenon is referred to as superparamagnetism [6, 7, 8, 9]. The particles align their magnetic moments in the presence of an applied magnetic field, but are immediately randomized by thermal agitation when the field is removed leaving no residual magnetization. The particles differ from paramagnetic species in having a magnetic moment on the order of $10^4 \mu_B$ per particle.

Ferrofluids are synthesized by placing the magnetic compound, surfactant, and carrier liquid in a ball mill half filled with steel balls, and grinding for 1-6 months [1]. The properties of the ferrofluid can be altered by using different carrier liquids, such as water, fluorocarbons, silicate esters, kerosine, and paraffin wax.

The ferrofluids have been characterized using a variety of physical methods including Mössbauer [10, 11, 12], magnetization measurements [13], and EPR [14].

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METAL VAPORIZATION: A ROUTE TO SOME NOVEL ORGANO-TRANSITION METAL CHEMISTRY

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April 5, 1979

Since the first report [1] of the reaction of transition metal vapors with organic compounds, research into synthesis using metal vapors has steadily expanded and has been the source of much fascinating new chemistry [2-4]. This technique [5] involves the generation of gaseous free metal atoms under high vacuum, and the low temperature condensation of these atoms with a large excess of an organic substrate vapor. Both static and rotating reaction vessels have been employed, and the latter has been adapted for the condensation of metal atoms into a cold solution of an involatile substrate in an inert solvent [6].

The vaporization method yields metal atoms in reactive high chemical potential states and, for this reason, has provided a convenient route to otherwise inaccessible organometallic systems. In particular, the incorporation of substituents possessing lone pairs of electrons into π -complexed arene rings had not been possible via the conventional Fischer-Hafner synthesis. Using metal vaporization, McGlinchey and coworkers have succeeded in making many fluorinated bis(arene)chromium complexes which undergo nucleophilic substitution and proton abstraction reactions [7]. Nucleophilic organometallic carbanions have been observed to form fluorinated polychromarenes [8] and have been used in the synthesis of bis(arene)chromium complexes containing a wide variety of organic substituents [9]. A new type of metal atom synthesis has been devised by Timms and coworkers [10], in which potassium atoms are condensed into a solution of a metal halide and an arene, forming bis(arene)metal complexes.

The oxidative addition of alkyl-halogen bonds to Pd atoms yields products which are too thermally unstable to observe [11]. However, Klabunde and Roberts obtained a novel η^3 -benzylpalladium-chloride dimer [12] upon the cocondensation of benzyl chloride and Pd atoms. Further studies [13] showed that the presence of aluminosilicate crucible insulation material produced organic free radicals which caused destruction of this dimer, as well as the isomerization and polymerization of alkenes.

Other recent examples of the applications of metal vapors in chemical synthesis are numerous and include the synthesis of a new $C_2B_5Co_2$ metallocarborane cluster [14], the synthesis of $M_4(CO)_4$ -(hexafluoro-2-butyne)₃ clusters ($M = Ni, Pd$) [15], the reaction of 1,3-butadiene with lanthanide atoms to form low-valent complexes [16], and the synthesis of $(C_6F_5)_2Ni(\eta^6\text{-toluene})$ [17] which has an exceedingly labile arene ligand. Many compounds formed by the metal vapor route have proven to be useful catalysts [2] and transition metal atoms themselves have been found to behave as efficient catalysts in a number of isomerization, hydrogenation, disproportionation, and polymerization reactions [2,18].

An important goal of organometallic chemistry in recent years has been the activation of saturated hydrocarbons. Skell and coworkers have reported the oxidative addition of C-C and C-H bonds of neopentane and isobutane to Zr atoms at low temperatures [19], an apparently unusual behavior among the metal atoms studied up to the present. Their hypothesis is supported by the nature of the products produced upon hydrolysis with D_2O .

Klabunde and coworkers have reported that codeposition of Ni vapor with weakly complexing solvents allows the formation of very reactive high surface area metal slurries and metal powders [20]. There is evidence [21,22] that alkane cleavage occurs at low temperature to form solvent fragment-stabilized Ni clusters. The metal particles can be tailored to have high catalytic activity or selectivity in hydrogenation and isomerization reactions [22] and highly dispersed catalysts have been obtained when metal atom solutions, formed by this method, are allowed to permeate catalyst supports [23].

The last decade has been an exploratory phase for preparative scale metal atom chemistry and there is growing interest in using the technique on a larger scale [24]. The variety of organo-transition metal compounds which have been prepared by the metal vaporization route illustrates the wide scope that this technique offers. Because of the accessibility of new chemistry, as well as its unique experimental advantages, metal vaporization will undoubtedly continue to gain importance as a widely-used synthetic approach.

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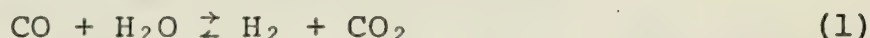
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HOMOGENEOUS CATALYSIS OF THE WATER GAS SHIFT REACTION

Robert Olsen

April 12, 1979

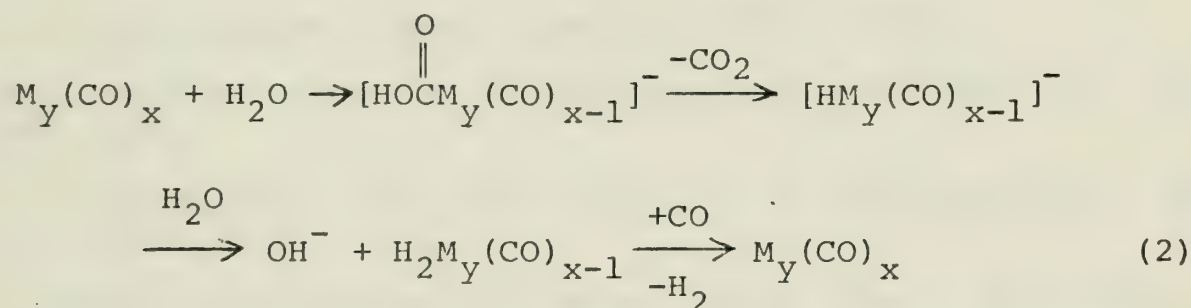
The water gas shift reaction (Eq. 1) is used extensively in industry today [1] to control the $H_2:CO$ ratio in various reactions [2].



Presently, two main heterogeneous systems are used to catalyze the water gas shift reaction. Homogeneous systems are being studied to find more economical and thermodynamically favored processes.

Metal carbonyls can be viewed as complexes containing carbon monoxide in an activated form. That is, a more positive charge on the carbonyl carbon makes it more susceptible to nucleophilic attack [3]. Thus, metal carbonyls are logical candidates for use as homogeneous catalysts for the water gas shift reaction.

Metal carbonyls react with water, presumably through a hydroxycarbonyl intermediate, to form CO_2 and a metal hydride [4-7]. The similarities between this reaction and the water gas shift reaction suggest a mechanism which can be used as a model system (Eq. 2) for the water gas shift reaction.



This model can be used as a basis of comparison for the different proposed mechanisms. It appears that the mono- and polynuclear metal carbonyl systems [8-11], such as $Fe(CO)_5$ [11] and $Ru_3(CO)_{12}$ [8-10], follow a reaction route similar to the proposed model. IR and NMR spectra of their reaction solutions indicate that a metal hydride is present. There is also evidence that a polyhydride species may be forming and that H_2 is reductively eliminated from this species in a rate-determining step.

Other systems may well follow rather different pathways. In mononuclear metal carbonyl systems under high CO pressure [12], supportive evidence has been found for CO displacement of the hydride as H^- from the metal center. The hydride could then react with water to form H_2 . The Group VI metal carbonyl systems are

found to lose activity after 20-25 turnovers [13]. This has been attributed to their forming a hydride-bridged dimer. In the PtL_3 system [14], metal hydride formation is thought to occur via trans addition of water across the platinum center. In both the $\text{K}_2\text{PtCl}_4/\text{SnCl}_4/\text{SnCl}_2$ [15] and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ [16] systems, hydride formation is thought to occur by way of H^+ addition to the metal center. Metal reduction would then take place in the CO_2 elimination step without any metal hydride formation.

In conclusion, numerous transition metal complexes have been found to catalyze the water gas shift reaction. The proposed mechanisms differ in minor respects from that shown in Equation 2. In all of these mechanisms, a hydroxycarbonyl intermediate is proposed from which CO_2 is expelled.

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STRUCTURAL STUDIES OF PROTEINS IN SOLUTION USING NMR
AND PARAMAGNETIC PROBES

James R. Stahlbush

April 19, 1979

The acquisition of structural information about proteins in solution is essential to our understanding of the biological activity of these proteins. In the past few years several researchers have turned to the use of paramagnetic probes in conjunction with nuclear magnetic resonance to obtain structural information about proteins in solution [1].

There are two types of paramagnetic probes. Relaxation probes such as Gd(III), Mn(II) and organic spin labels broaden the NMR resonances of nuclei near the probe. The broadening, $\Delta\nu$, is inversely proportional to r^6 , where r is the distance between the perturbed nuclei and the probe. Shift probes such as all the Ln(III) ions except Gd(III), La(III), and Lu(III) shift NMR resonances of nuclei near the probe. The shifting, $\Delta\delta$, is inversely proportional to r^3 and is also dependent on the angular orientation of the perturbed nuclei in relation to the probe's magnetic axis[2]. Thus the degree to which a resonance is changed indicates the relative position of the perturbed nuclei with respect to the probe.

The addition of a paramagnetic probe to a protein changes only a small percentage of the NMR resonances. Comparison of the perturbed spectrum to the normal spectrum (Paramagnetic Difference Spectroscopy [3]) results in the assignment of NMR resonances to specific types of amino acid residues which are near the probe [4].

R. J. P. Williams and coworkers have extensively studied lysozyme using lanthanide ions as paramagnetic probes [4-6]. By studying the shift of methyl resonances perturbed by the shift probe Yb(III) at various pH values the lanthanide ions were proposed to bind simultaneously to the glutamic acid-35 and aspartic acid-52 residues [6]. The same binding site was observed in the crystal structure done by Imoto and coworkers [7]. This binding site is the active site of lysozyme which hydrolyzes glycosidic linkages of certain bacterial cell walls. Thus R. J. P. Williams and coworkers were able to map out the position of twelve amino acid residues within 15-20Å of the active site [4-6] using the broadening probe, Gd(III), and various other lanthanides as shift probes. These NMR results were in good agreement with the crystal structure results [7] indicating that there are few differences between the two forms of lysozyme.

Brewer and coworkers have studied the binding of ^{13}C -enriched saccharides to Concanavalin A (ConA) using ^{13}C NMR [8,9]. ConA has two metal sites per monomer, one Ca^{2+} site and one transition metal atom site. Comparison between the T_1 values of the saccharide carbon atoms when bound to the paramagnetic Mn(II)-ConA derivative

versus the diamagnetic Zn(II)-ConA derivative indicated that the saccharide was bound approximately 10Å from the transition metal ion site. This result contrasted with a preliminary crystal structure [10] estimate of 20-23Å; however, a more recent crystal structure [11] agrees with the NMR results.

Lanir and Navon have also used ^{13}C NMR to study the binding of acetate ions to carbonic anhydrase [12] which is a zinc containing enzyme. By substituting Mn(II) for the Zn(II), the distance between the metal site and bound acetate ion was calculated to be 4.5Å. The nine histidine resonances in the ^1H NMR spectrum were classified into three categories by comparing the resonances of the zinc analog to the paramagnetic cobalt(II) analog at various pH values [13]. Three histidine residues were identified as ligands of the metal, three within the active site and three on the surface of the enzyme.

Finally Dwek and coworkers [14,15] examined the active site of the Fv portion of the myeloma protein MOPC-315 using organic spin labels. Three conclusions were drawn from their studies. First, there are no major conformational changes upon the spin label binding to the antibody. Second, there are a relatively large number of aromatic amino acid residues at the binding site. Third, two of three histidine residues in the protein are near the binding site. The NMR results were compared to model building studies by Padlan and coworkers [16].

In conclusion, the use of paramagnetic probes with NMR allows structural information about proteins to be determined in solution. The major drawback of this technique is that presently only amino acid residues with aromatic or methyl groups can be successfully indentified and assigned.

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SEMICONDUCTING RARE EARTH METALS

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Semiconducting rare earth (RE) compounds have been known for less than twenty years. Early studies were plagued by a constant problem: purity. Extremely pure samples are required for meaningful measurements. Researchers are still unable to prepare stoichiometric pnictides but success has been obtained in the preparation of RE hexaborides and chalcogenides.

Until recently it was thought that ferromagnetism was restricted to crystalline metals and alloys. However, many of the europium semiconductors have exhibited ferromagnetic ordering and other RE semiconductors have exhibited anti-ferromagnetic ordering. The interesting magnetic properties have made the RE chalcogenides and hexaborides heavily studied systems.

Theoretical work has shown that hexaborides of RE^{+3} ions will be metallic while hexaborides of RE^{+2} ions will be semiconducting [1]. Optical, magnetic, and electrical studies have shown that only EuB_6 and YbB_6 are semiconducting at room temperature [1,2]. EuB_6 is interesting because it is the only ferromagnetic hexaboride [1,3]. All other hexaborides are antiferromagnetic (LaB_6 is paramagnetic and YbB_6 and SmB_6 are nonmagnetic). The only other semiconducting hexaboride is SmB_6 which is a nonmagnetic semiconductor at low temperatures [4,5]. Mössbauer results show an isomer shift for SmB_6 which is between those for SmF_2 and SmF_3 [4]. Since SmB_6 is a semiconductor, there can be no Sm^{+3} ion. It was thus postulated that SmB_6 has two electronic configurations in its semiconducting phase: $4f^6 5d^0$ and $4f^5 5d^1$ [4].

The europium monochalcogenides are the most heavily studied of the RE compounds [6-11]. Only europium and thulium monochalcogenides exhibit any magnetic order. The europium monochalcogenides order both ferro- and antiferromagnetically while thulium telluride orders antiferromagnetically [7]. Samarium monochalcogenides are also very interesting because they undergo pressure induced semiconductor-to-metal phase transitions [5,12,13]. The electronic structure of SmS is also similar to that of SmB_6 .

RE sesquioxides and sesquisulfides are also semiconductors with the interesting fact that they are also mixed-valence semiconductors [14,15]. Finally, Eu_3S_4 also exhibits mixed-valence semiconducting properties and appears to undergo conduction by an electron-hopping process [16,17].

Although no longer seriously considered for practical semiconductor devices, RE compounds still provide very good semiconductor models due to their interesting and sometimes unique electric, magnetic, and optical properties.

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SUPPORTED METAL CARBONYL CLUSTERS

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As our energy demands increase and resources decrease, the development of more efficient chemical processes is essential. These new developments may reside in the discovery of new catalysts. Recently, there have been attempts to correlate relationships between homogeneous and heterogeneous catalysts. Studies of metal clusters have begun with the hope they may serve as models for metal surfaces [1,2]. Known homogeneous catalysts have been "heterogenized" by attaching these catalysts to polymeric supports [3,4]. These two concepts have been combined through the investigation of polymer-bound clusters. Supported metal carbonyl clusters offer several advantages. Interactions that lead to aggregation of the metal are minimized. Thus, after decarbonylation, it might be possible to obtain a coordinatively unsaturated species whose particle size may be controlled by using the appropriate cluster precursor.

The reactivity of a metal carbonyl cluster with polymeric supports was studied using $\text{Rh}_6(\text{CO})_{16}$. Bassett and Smith investigated the reaction of this cluster with silica gel [5]. They found the terminal carbonyl groups were oxidized by surface water or hydroxide groups. The original cluster could be regenerated with CO pressure. These workers also investigated to what extent the cluster could be decarbonylated while maintaining its integrity. K. L. Watters and coworkers studied the reactivity of $\text{Rh}_6(\text{CO})_{16}$ on alumina [6]. A gradual decarbonylation of the cluster is catalyzed by the alumina surface. The cluster most likely retains its integrity since it can be regenerated with CO. Reaction of $\text{Rh}_6(\text{CO})_{16}$ with triphenylphosphine has been investigated in solution as well as with the polymer bound analog [7,8]. There is general agreement that the species present on phosphinated polystyrene is $\text{Rh}_6(\text{CO})_{13}(\text{PPh}_3)_3$, where the cluster integrity has been maintained [8,9]. Jarrell and Gates investigated the IR and kinetics of this species for olefin hydrogenation. Cyclohexene hydrogenation was second order in olefin and half order in hydrogen. The ligands present on the functioning catalyst were inferred to be hydride, hydrocarbon, and polymer-attached phosphine groups. CO acted as an inhibitor in the catalytic reaction. The same workers also investigated the aggregation of the metal cluster using trace amounts of oxygen in the feed stream [10]. The phosphine groups were oxidized allowing the Rh to agglomerate and slowly forming a supported catalyst containing Rh crystallites about 20 Å in diameter. These were characterized by IR and electron microscopy. $\text{Rh}_6(\text{CO})_{16}$ has also been immobilized onto phosphinated silica gel [11]. The tetranuclear Ir carbonyl cluster was found to maintain its integrity when bound to phosphinated polystyrene [12,13].

Interesting catalysts have been prepared from metal carbonyl clusters. Ichikawa studied the catalytic properties of $[\text{Cp}_2\text{Ni}_2(\text{CO})_2]$ and $[\text{Cp}_3\text{Ni}_3(\text{CO})_2]$ on silica gel [14]. ESR results suggest the trinickel complex maintained a three atom center on the silica after decarbonylation. The catalyst was active for the hydroformylation of ethylene in low yields, whereas a catalyst prepared from $\text{Ni}(\text{Cp})_2$ was not. Ichikawa also prepared highly dispersed Pt aggregates by the pyrolysis of Pt_{15} - Pt_3 anion clusters [15]. Pt aggregates were active catalysts for the dehydrocyclization of n-hexane. Systematic trends in selectivity of products were observed with the size of the cluster precursor. Basset and Ugo found hydrocarbon formation occurred with subsequent heating of a metal carbonyl cluster with an inorganic support [16]. Surface water was confirmed as the source of H_2 through D_2O exchange. Soon thereafter, Ichikawa reported the synthesis of methanol and ethanol over catalysts prepared by pyrolysis of metal clusters on various metal oxides [17,18,19]. Catalytic properties of the supported metal crystallites were found to depend remarkably on the cluster precursor and the type of support. Increased catalytic activity was demonstrated by these catalysts when compared to conventional Rh metal catalysts. H. B. Gray and coworkers have prepared active hydroformylation catalysts by the photolysis of either $\text{Rh}_4(\text{CO})_{12}$ or $\text{Co}_4(\text{CO})_{12}$ solutions in the presence of polyvinylpyridine [20]. Rates were found to be comparable to those achieved by industrial Rh catalysts under more drastic conditions. Ichikawa as well has reported a hydroformylation catalyst using his pyrolysis method [21].

In summary, $\text{Rh}_6(\text{CO})_{16}$ was reacted with various polymeric supports to determine what reactions may occur between metal clusters and these supports. Novel catalysts have been prepared through polymer attachment of metal clusters. Activity of these catalysts was found to depend on the cluster precursor and the support.

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ELECTRON DYNAMICS OF METAL-QUINONE COMPLEXES

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Quinones play an integral role in many biological electron transfer processes, particularly respiration and photosynthesis [1]. During these processes, quinones are reversibly reduced to semiquinone radical anions, with the concomitant oxidation of divalent metal centers. Para-quinones, as exemplified by ubiquinone, have been found to transfer electrons via the semiquinone form from the high potential iron sulfur protein Hipip to the cytochromes [2]. Ortho-quinones, as totally reduced catechols, function as reducing agents in enzymatically catalyzed insertion and non-insertion reactions whereby O_2 is reduced to H_2O [1,3].

A priori to the understanding of these electron transfer reactions is the fundamental apperception of the reduction-oxidation characteristics of the quinone and the nature of metal-quinone interactions. The redox function of the quinone has been well established [4]. However, relatively few investigations of quinones reacting with divalent metal ions have been reported [4,5]. To elucidate the electronic and molecular structure of metal-quinone complexes, a series of para-quinones and ortho-quinones was reacted with $M^{II}(\text{salen})$, where $M = \text{Fe}, \text{Mn}, \text{Co}$ and salen is N,N' -ethylenebis(salicylideneimine), and $\text{Fe}^{II}(\text{TPP})$, where TPP is tetraphenylporphine.

The reduction of para benzenoid quinones, such as p-benzoquinone and duroquinone, to the dianion of the hydroquinone was accomplished with $\text{Fe}^{II}(\text{salen})$. This reaction, first reported by Floriani, yields bridged compounds of the type $(\text{salen})\text{Fe}^{III}\text{-Q-Fe}^{III}(\text{salen})$ [6,7]. The quinone undergoes a two electron reduction to the dianion, as each ferrous ion is concurrently oxidized to the high spin trivalent state. These complexes are characterized as dimeric, square pyramidal systems exhibiting weak antiferromagnetic exchange interactions with J values ranging from -0.2 cm^{-1} to -5.9 cm^{-1} . Infrared data substantiate the reduction of the quinone while Mössbauer spectra confirm the oxidation of the iron. Several unhindered p-quinones have been reacted with $\text{Fe}^{II}(\text{TPP})$ to form similar bridged systems displaying slightly larger J values [8]. Mn^{II} and $\text{Co}^{II}(\text{salen})$ also react in this manner, but only with high potential quinones.

Metal complexes ligated by semiquinones have been prepared by oxidative addition in a manner similar to the synthesis of para-quinone complexes. $M^{II}(\text{salen})$, where $M = \text{Fe}, \text{Mn},$ and Co , and various orthoquinones react via a one electron transfer process to form $M^{III}(\text{salen})\text{Q}$ systems [9,10]. Complexes of 9,10-phenanthrenequinone, 3,5-di-tert-butyl-o-benzoquinone, and 1,2-naphthoquinone have been synthesized. Chemical and EPR data suggest that coordination of the semiquinone occurs through both oxygen

atoms [10,11]. Mössbauer spectra clearly establish the oxidation state of iron as +3 high spin. Complete coupling of the radical anion electron, residing in a semiquinone π molecular orbital, with an iron d orbital electron results in a net $S = 2$ spin system exhibiting a room temperature μ_{eff} of 4.85 B.M. A similar anti-ferromagnetic exchange is found for $\text{Mn}^{\text{III}}/\text{salen}/\text{Q}$ complexes. In the case of cobalt complexes, X-band EPR data confirm the oxidation of the cobalt, with the unpaired electron spin residing on the semiquinone moiety. Attempts to isolate a semiquinone coordinated to $\text{Fe}^{\text{II}}(\text{TPP})$ proved unsuccessful. Reactions of various ortho-quinones with the ferrous porphyrin yielded a mixture of high spin ferric material and $[\text{Fe}(\text{TPP})]_2\text{O}$. While redox occurs, stabilization of the semiquinone is not accomplished, presumably because the stereochemical requirement for quinone coordination is not met. The semiquinone complexes disproportionate, forming 2:1 metal-hydroquinone systems and free quinone. Magnetic susceptibility data on $[\text{Fe}(\text{TPP})]_2\text{O}$ -chloranil and $[\text{Fe}(\text{salen})]_2\text{-o-chloranil}$ suggest the two trivalent metal ions are coordinated to separate oxygen atoms.

By reacting orthoquinones with $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$, a series of neutral tris-semiquinone complexes has been prepared [12]. As with the 1:1 metal-semiquinone systems, magnetic susceptibility data indicate a strong antiferromagnetic exchange interaction between metal d electrons and semiquinone unpaired electrons. Iron tris ligated with 3,5-di-tert-butyl-o-benzoquinone exhibits a magnetic moment of 2.90 B.M. at room temperature, suggesting complete coupling of the 3 ligand based electrons with 3 electrons derived from iron orbitals. Structural data on a related complex confirm the presence of semiquinone ligands and suggest a plausible pathway for extended intermolecular interactions.

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A MAGNETIC AND MÖSSBAUER STUDY OF SOME MIXED VALENCE COMPOUNDS

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Final Seminar

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Magnetite, Fe_3O_4 , is the mixed valence mineral commonly used as the material for compass needles. It was discovered by Briggs and Kjargaard [1] that when iron salts were reacted in a lignosulfonate matrix (lignin is a major component of wood), an iron oxide was formed that had interesting magnetic properties. Magnetic and Mössbauer studies of several different samples of this material confirm that the microparticles formed are magnetite. These particles are small enough to consist only of single domains, and behave superparamagnetically. When observed on the very fast ($\sim 10^{-7}$ sec $^{-1}$) Mössbauer timescale, the thermal magnetic relaxation of the magnetite is such that some of the particles show a superparamagnetic doublet, while other particles which relax more slowly give a complete magnetic hyperfine spectrum. The ratio of these two types of hyperfine changes with the particle size and the temperature of the experiment. The average particle size is larger in those samples with a greater percent of iron. This is reflected by an increased magnetization and larger amount of magnetic hyperfine in the Mössbauer spectrum.

The organometallic compounds diferrocenylketone (DFK) and triferrocenyldiketone (TFK) form mono- and dioxidized compounds, respectively. Unlike many ferrocene compounds studied, the relative intensities of the quadrupole split doublets (corresponding to the ferrocene and ferricenium portions of the compound) in these Mössbauer spectra do not have integral ratios. This means that the two types of iron centers do not have identical absorption of gamma rays, i.e., their recoil free fraction (rff) is different. This is unusual since intermolecular vibrations generally make the most important contribution to the rff. Similar phenomena have been observed previously, but it was assumed in those cases that there was a migration of the electron density, causing the ratios of the peaks to change with temperature. It had been assumed that the recoil free fraction of ferrocene and ferricenium moieties would be similar in different compounds. Studies of some physical mixtures show that this is not the case. Since the rff of ferrocene as a function of temperature has been determined [2], the relative area of the ferrocene peaks in these mixtures was used to find the rff of three ferricenium salts. These were found to differ substantially from the values calculated for ferrocene.

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THE NATURE OF ACTIVE SITES IN CATALYTIC ZEOLITES

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May 11, 1979

Zeolites are crystalline aluminosilicates consisting of an ordered framework structure forming a network of cavities interconnected by pores of molecular dimensions. Positively charged ions and water molecules reside in these cavities and can move about freely during cation exchange and dehydration.

There are a number of uses of zeolites in areas as diverse as pollution control, energy conservation and agriculture. Applications in these areas range from oil spill cleanups to animal nutrition. Undoubtedly, however, the use of zeolites in petroleum refining is the most important and significant application of zeolites at this time.

Despite the widespread use of zeolites a number of important questions regarding zeolitic behavior remain unanswered. The two most significant areas of doubt concern

- (1) The nature of the metallic sites in zeolites and
- (2) The role of protons in zeolites.

An incomplete list of zeolite books [1-5] and review articles [6-10] is given in the list of references.

The zeolite ZSM-5 is particularly interesting because it catalyzes the transformation of methanol into gasoline hydrocarbons [11-13]. This zeolite is not commercially available but can be synthesized [14]. Very little is known about ZSM-5 and therefore we have chosen to study its thermal, ion exchange, electronic and chemical properties.

Europium exchanged zeolites are of interest because the rare-earth-exchanged zeolites are important as catalysts and because the crystallinity of the zeolites provides cation sites of a definite symmetry. A single crystal X-ray structure of europium exchanged zeolite A has been reported and the presence of Eu^{4+} has been postulated [15,16]. In addition, a process has been reported for thermolytically dissociating water using europium exchanged zeolites [17]. It is believed that the conversion of europium to the 2+ and 3+ oxidation states is important in this thermolytic cycle. By using Mössbauer [18], EPR, luminescence lifetime [19] and EXAFS [20] spectroscopy we investigated the nature of the europium sites in zeolites A, X, Y and ZSM-5 as a function of hydration and chemical treatment.

A recent X-ray photoelectron spectroscopy study of zeolites has indicated that there are major differences between the surface and the bulk composition of zeolites [21]. Such a compositional differentiation may be important in determining the selectivity of a particular zeolite. Single crystal and powdered zeolites have been subjected to Auger electron spectroscopic analysis in order to investigate this problem. In addition, AES has been used to observe changes in metal ion concentrations on zeolites as a function of dehydration in hopes of observing metal reduction and migration.

Finally, the isomerization of 1-butene catalyzed by various europium zeolites will be described. It is extremely important to study catalytic processes on well characterized systems. Systematic observations of the catalysis of this reaction may lead to a greater understanding of the active sites in zeolites. Factors of importance for this reaction are silica-alumina ratio of the zeolite, extent of europium exchange, temperature of activation, activation pretreatment, structural integrity of the zeolite, cation migration, impurity levels and the reactivity of unexchanged zeolites.

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NUCLEAR QUADRUPOLE RESONANCE STUDIES OF
METAL COMPLEXES OF BIOLOGICAL INTEREST

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May 15, 1979

The importance of metal ions in biological systems has been well established [1]. Zinc plays an important role as a Lewis acid in metalloenzymes such as carboxypeptidase and carbonic anhydrase. It is, therefore, important to understand the nature of the interaction between zinc and biological model ligands such as imidazole, amino acids, and peptides. Nuclear quadrupole resonance spectroscopy [2] has proven to be a useful technique for the study of the interaction between diamagnetic metal ions and nitrogen donor ligands.

The probe employed in this study is the quadrupolar nucleus, ^{14}N , for which $I=1$. The separation between the quadrupolar energy levels is determined by the orientation dependent interaction of the nitrogen nucleus with its electronic environment. The electric field gradient (efg), which determines the energies, may be factored into contributions arising from electrons in molecular orbitals and charges on neighboring nuclei. An approximate method formulated by Townes and Dailey [3] which ascribes the efg solely to nitrogen valence p-electrons has been successfully employed. Information about the bonding of nitrogen with metal ions may be obtained by relating efg data to populations of hybrid orbitals centered on nitrogen.

Difficulties in detecting nitrogen quadrupolar transitions in the region from 0 to 2 MHz may be overcome by use of the double resonance by level crossing (drlc) technique [4]. In this technique, an abundant spin species such as protons is initially polarized in a large static magnetic field. During transit of the sample to a zero field region, the quadrupolar spin system equilibrates with the proton spin system by spin exchange during level crossing. The sample is irradiated with a radio frequency magnetic field in the zero field region and returned to the high field region, again undergoing level crossing exchange. The magnitude of the proton magnetization is then detected by a wide-line NMR experiment. If the irradiation frequency corresponds to a quadrupolar transition frequency, energy is resonantly absorbed by the nitrogen nuclei and transferred to the proton spin system during the second level crossing. Transitions are, therefore, manifested as a decrease in the magnitude of the proton magnetization.

The interactions of Zn and Cd with imidazole as a function of coordination environment have been studied using the drlc technique [5]. The nitrogens are assumed to be sp^2 hybridized, as were those of a previous pyridine study [6]. If it is assumed that the two N-C σ -bonds are equivalent, the efg components may be expressed in terms of orbital populations, σ , a , and b , which refer

to the populations at nitrogen of the donor or lone pair orbital, the π -orbital, and the C-N σ -bond orbital, respectively. Coordination to a metal should decrease the donor orbital population from that of the free ligand and concomitantly produce an inductive response in the other orbitals as follows:

$$a = a_0 + A(2 - \sigma)$$

$$b = b_0 + B(2 - \sigma)$$

when 2, a , and b are the populations in the reference compound, N-benzylimidazole. The values of the scaling factors, A and B , are based upon experimental NQR data. From the calculated values of the efg components as a function of σ , it is possible to relate experimentally determined efg's to changes in the donor orbital population at nitrogen and, therefore, the extent of electron donation to the Lewis acid center. For the imino(N3) nitrogen, several general observations can be made. Charge withdrawal from N(3) is lower in six-coordinate than in four-coordinate metal complexes. Zinc withdraws more charge from nitrogen than does cadmium in analogous metal complexes. The extent of charge withdrawal in four-coordinate complexes varies with the nature of the other ligands bound to the metal. Imidazole and its anion differ in their extent of donation to a metal ion [7]. For the amino(N1) nitrogen, the population of the donor orbital, which is involved in the N-H bond, is determined primarily by intermolecular interactions, particularly those involving hydrogen bonding. In addition to quantitative information about orbital populations, structural information may be obtained [8].

The interactions of Zn and Cd with the $-\text{NH}_2$ group of amino acids and peptides have also been studied using NQR spectroscopy [9]. The model employed for sp^3 nitrogen is a modification of that employed by Edmonds, *et al.* [10]. The N-H bonds are assumed equivalent resulting in a plane of symmetry. The populations at nitrogen of the orbitals forming the two identical N-H, N-C, and third N-H (or N-M) bonds are defined as a , b , and c , respectively. Upon coordination, the third hydrogen of the zwitterion is replaced by the metal ion, changing the population, c . A concomitant change occurs in the other orbitals as given by the following equations:

$$a = a_0 + A(c - c_0)$$

$$b = b_0 + B(c - c_0)$$

The values of the scaling factors, A and B , are chosen to be consistent with those of the previous imidazole study. Values for the components of the efg are calculated as a function of the population change, $(c - c_0)$. Values of $(c - c_0)$ for metal-peptide and metal-amino acid complexes are derived by fitting the experimentally determined efg to the calculated curves. These values may be interpreted in terms of the metal-nitrogen interaction.

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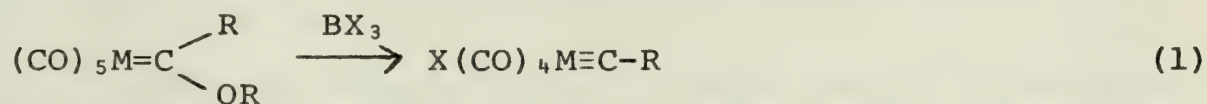
THE METAL-CARBON TRIPLE BOND

Allen D. Clauss

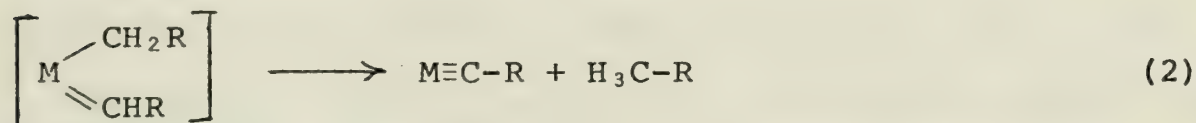
May 17, 1979

The first compounds containing a metal-carbon triple bond were reported by E. O. Fischer in 1973 [3]. Since that time, over one hundred compounds of this type have been characterized. The reactivity of these compounds, however, remains relatively unexplored [1-12].

The first carbyne* compounds synthesized by Fischer and co-workers were derived from the well known heteroatom-stabilized carbene complexes [7]. They found that treatment of the carbenes with boron trihalides resulted in halide substitution at the metal center and loss of the lone pair stabilizing group as an anion to give thermally unstable carbyne complexes (eq. 1) [3].



M = Cr, Mo, W



Alkylidyne compounds of greater thermal stability have been prepared by Schrock and coworkers [8-12]. In general, these compounds arise from α -hydrogen abstraction from a sterically crowded, mixed alkyl-alkylidene intermediate with concomitant elimination of alkane (eq. 2) [8,9,11]. The first examples of this type were tantalum and niobium neopentylidyne and benzilidyne complexes [8,9]. Recently, Schrock has reported neopentylidyne compounds of molybdenum and tungsten by a similar method [12].

Although relatively little work has been reported concerning the reactivity of carbyne compounds, recent work by Kreissl and Stone has demonstrated interesting and diverse reaction pathways for these compounds [13-15]. Kreissl and coworkers have shown that Fischer-type carbyne complexes of molybdenum and tungsten can be carbonylated under very mild conditions to give a high yield of the corresponding metal substituted ketene [13]. More recently, Stone and coworkers have reported the addition of a zero-valent platinum center across the metal carbon triple bond in a Fischer-type tungsten carbyne to give the mixed metal dimer with a bridging carbyne ligand [15].

*The terms carbyne and alkylidyne are both used to a considerable extent in the chemical literature in reference to compounds containing a metal carbon triple bond. There is no clear distinction between the two terms and they may be used interchangeably.

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MAGNETIC EXCHANGE INVESTIGATIONS OF TRANSITION METAL COMPLEXES

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May 22, 1979

Polynuclear complexes of Ti(III) and Cu(II) are amenable to investigation by EPR and magnetic susceptibility techniques. Such studies coupled with molecular orbital analyses can provide important data bearing on the location of unpaired electron density in a complex, the facility of electron transfer, and the orbital pathways of electron transfer.

By virtue of their reactivity, low valent titanium complexes have experienced much interest. Recently, bis(η^5 -cyclopentadienyl)-dicarbonyltitanium(II) has been found to react with small molecules including CO_2 , promoting its disproportionation to CO_3^{2-} and CO [1]. Bis(η^5 -cyclopentadienyl)titanium(II) and the zirconium analog reduce dinitrogen to ammonia and hydrazine [2]. TiCl_4 and various alkoxide modifications are reduced by a trialkyl aluminum to form the fibrous Ti(III) active species of the Ziegler-Natta catalyst, important in olefin polymerization [3]. A study of the reactivity and electronic nature of low valent titanium compounds may contribute to the overall understanding of the chemistry of this element.

Complexes of bis(η^5 -cyclopentadienyl)titanium(III) and various dicarboxylic acids have been prepared. The compounds do not exhibit an appreciable magnetic exchange interaction in the variable temperature magnetic susceptibility experiments. EPR studies, however, indicate that an exchange interaction is propagated through the various bridging units which consist of aliphatic straight chain and cyclic dicarboxylic acids and phthalic acids. This is in agreement with recent EPR evidence that nitroxyl biradicals bridged by these moieties experience such spin exchange [4]. Our results corroborate a recent proposal that a Co (III) binuclear complex, bridged by one carboxylate end of a dicarboxylic acid, is reduced by Ti(III), which complexes to the free end of the acid and transfers its electron through the carbon chain [5].

Various pyrimidines and related compounds including sulfur containing compounds have been successfully complexed to bis(η^5 -cyclopentadienyl)titanium(III) [6]. The magnetic susceptibility and EPR behavior are quite different upon comparison of the oxygen and sulfur analogs [7]. The occurrence of low lying excited states in the sulfur compounds and slight structural changes in the bond angles and bond distances from the oxygen to sulfur compounds may provide the explanation for the unusual behavior.

Transition metals have been investigated for their role in polymeric linear chains in the quest for new semiconductors. Variable temperature magnetic susceptibility experiments have shown that Cu(II), Fe(II), and Fe(III) dihydroxyquinone polymers exhibit antiferromagnetism characteristic of linear chains [8]. Because of the uncertainty in determining exchange parameters for polymeric compounds, especially those that are not structurally characterized, it is of interest to investigate the magnetic exchange present in discrete binuclear



metal complexes, which have the same bridging units found in the polymers.

Copper(II) and nickel(II) dihydroxyquinone complexes have been prepared. EPR and magnetic susceptibility investigations have elucidated the structure and bonding of these complexes. The viability of the various dihydroxyquinone dianion bridging units for propagating magnetic exchange interactions has been compared with the characteristics of the oxalate and squarate dianions [9].

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BASE CATALYSIS OF LIGAND SUBSTITUTION IN METAL CARBONYLS

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Metal carbonyls are likely to be important species in catalytic processes involving carbon monoxide, and therefore their reactions are of interest.

There are two ways in which metal carbonyls can react with nucleophiles:

The first is ligand substitution, which normally proceeds via a rate-limiting ligand loss with subsequent rapid attack of the nucleophile on the coordinatively unsaturated metal center [1,2].

The second is attack of a nucleophile at the carbonyl carbon to give an adduct of the carbonyl and the nucleophile as a new ligand [3,4].

$\text{Mn(CO)}_5\text{CH}_3\text{CN}^+$ appears to undergo substitution reactions via nucleophilic attack at CO. This species is known to undergo nucleophilic attack at CO [5,6]. The substitution mechanism can be understood in terms of the altered electronic properties of the new ligand, the adduct-ligand, formed by the attack of the nucleophile at the CO carbon, relative to CO, which can have a profound effect on ligand lability in the metal carbonyl [7].

This reaction has been observed in two solvent systems. In nitromethane it appears that attack of the conjugate base of the solvent on coordinated CO occurs. Rapid substitution at the metal follows as a result of the labilizing power of the adduct-ligand. The product is $\text{Mn(CO)}_3\text{L}_3^+$ and a mole of CO_2 is liberated per mole complex. The rate depends on both the nature and concentration of L.

In solvents where conjugate base formation is unlikely (e.g., acetonitrile) it was observed that while triphenylphosphine reacts by a dissociative pathway, pyridine reacts much faster and the rate depends on pyridine concentration. This can be interpreted in terms of direct attack by pyridine at the CO carbon. This adduct-ligand labilizes the metal complex towards substitution.

The concept of adduct-ligands derived from CO imparting labilization to metal carbonyl complexes has applications to some catalytic processes. Both the phase-transfer catalysed substitution reactions of group VI metal carbonyls [8] and the iron pentacarbonyl catalyzed water-gas shift reaction [9] can be explained using this concept.



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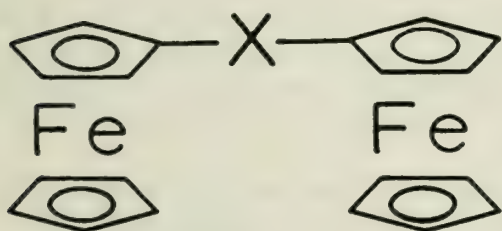
ELECTRON TRANSFER IN MIXED VALENCE METALLOCENES

Jack A. Kramer

May 29, 1979

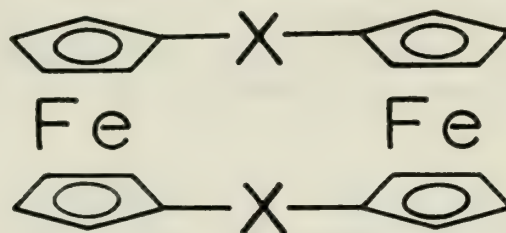
Electron transfer is an integral part of many chemical, electrochemical, and biological processes. In particular, inner and outer sphere electron transfer reactions and biological electron transport chains involved in metabolism, nitrogen fixation, and photosynthesis have received considerable attention. Mixed valence compounds [1,2], which contain two or more metal atoms in different oxidation states, have been found useful in unravelling the intricacies of these electron transfer reactions. Knowledge of the factors which influence electron transfer in mixed valence compounds should be applicable to understanding these same phenomena in more complicated systems.

Bridged ferrocenes (I, II) are ideal compounds for the study [3-5] of mixed valence interactions because of their structural and electronic variability, stability in a variety of oxidation states, and well characterized ferrocene and ferricenium electronic ground states. They are also amenable to study by such techniques as EPR, IR, NMR, electronic, and ^{57}Fe Mössbauer spectroscopies, and variable temperatures magnetic susceptibility.



I

- a. $\text{X} = -\text{C}\equiv\text{C}-$
b. $\text{X} = -\text{Se}-$



II

- a. $\text{X} = -\text{C}\equiv\text{C}-$

By varying the structure of the bridged ferrocene unit and determining the rate of electron transfer by the use of various physical techniques, information pertaining to the different requirements of the direct and superexchange electron transfer mechanisms may be obtained.

The unpaired electron of the bisfulvalene dicobalt monocation [6] is directed toward the bridging ligand, while that of the bisfulvalene diiron monocation (Class III, delocalized) is directed toward the other iron. If the rate of electron transfer were much



less in the cobalt case, then the direct mechanism of electron transfer must be dominant. However, optical and EPR studies show that the electron of the cobalt compound is also delocalized.

The mixed valence cation of diferrocenyl selenide [7] (Ib) was found to be a Class I (noninteracting) mixed valence compound. No intervalence transfer (IT) band was seen in the electronic spectrum, and the ^{57}Fe Mössbauer spectrum [8] exhibits separate absorptions due to the ferrocene and ferricenium portions of the molecule. An Fe-Fe distance of 6.06 Å was derived from the X-ray structure of $\text{DFSI}_3 \cdot \text{I}_2 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$. Comparison of this distance with those of ferricenyltris(ferrocenyl)borate [9], a Class II (weakly interacting) mixed valence compound, leads to the conclusion that the maximum distance for appreciable direct electron transfer is between 5.35 and 6.06 Å.

In an effort to establish a similar limit for superexchange, diferrocenylacetylene was prepared and oxidized. Although the mixed valence cation could be generated electrochemically [10], chemical oxidation produced only the dioxidized species. Variable temperature magnetic susceptibility measurements showed that there is a 3 cm^{-1} interaction between the two Fe(III) ions. This complements the finding that the monocation is weakly interacting [10,11].

[2.2]ferrocenophane-1,13-diyne (IIa) was prepared to attempt to increase the amount of interaction, analogous to the biferrocene-bisfulvalene diiron case. The mixed valence ion was found to have equivalent iron sites on the timescales of ^{57}Fe Mössbauer, EPR, and IR spectroscopies [10-12]. Because of the long Fe-Fe distance (≈ 6.5 Å) in this compound, superexchange must be responsible for this large interaction. In order for this superexchange to occur, the bridged cyclopentadienide groups must be coplanar for maximum overlap of the pi systems.

A correlation was found between the quadrupole splittings of the ^{57}Fe Mössbauer spectra of various oxidized mono- and binuclear ferrocene compounds and the g anisotropies observed in the EPR spectra. It is proposed [12] that the orbital angular momentum of the unpaired electron is being quenched by distortion and/or delocalization, with a corresponding redistribution of electrons among the Fe 3d orbitals, which is reflected by the quadrupole splitting.

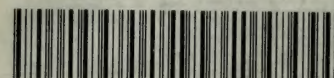
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